LBNL-1246E

ERNEST ORLANDO LAWRENCE
BERKELEY NATIONAL LABORATORY

Insecticide Exposures on Commercial Aircraft: A Literature Review and Screening Level Assessment

R.L. Maddalena and T.E. McKone

Environmental Energy Technologies Division

October 2008

Research Supported by:

U.S. Federal Aviation Administration

Insecticide Exposures on Commercial Aircraft: A Literature Review and Screening Level Assessment

R.L. Maddalena[1] and T.E. McKone[1,2]

[1]Indoor Environment Department
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720

[2]School of Public Health
University of California
Berkeley, CA 94720

October 2008

This work was supported by the U.S. Federal Aviation Administration (FAA) Office of Aerospace Medicine through the Air Transportation Center of Excellence for Airliner Cabin Environment Research (ACER) Cooperative Agreement 04-C-ACE-UCB, and carried out at the Lawrence Berkeley National Laboratory (LBNL) under U.S. Department of Energy (DOE) Contract Grant No. DE-AC02-05CH11231. We thank William Nazaroff, University of California, Berkeley (UCB), for serving as UCB research manager and for providing the interface with the FAA and the ACER. We are grateful to David Space and Fue Vue, Boeing Company, for valuable input during development of the passive samplers and to Agnes Lobscheid, LBNL, and Judith Murawski, Association of Flight Attendants-CWA, AFL-CIO, for their careful reviews. We also thank our FAA project managers, Jean Watson and Nancy Claussen, for guidance and input throughout this research.

This page intentionally blank

Abstract

The objective of this project was to provide initial estimates of the relationship between insecticide use on passenger aircraft and exposure levels present in the cabin environment. The work was initially divided into three tasks including 1) a review of insecticide application practices in commercial aircraft, 2) exploratory measurements of insecticide concentrations in treated aircraft and 3) screening level exposure modeling. Task 1 gathered information that is needed to assess the time-concentration history of insecticides in the airline cabin. The literature review focused on application practices, information about the cabin environment and existing measurements of exposure concentrations following treatment. Information from the airlines was not available for estimating insecticide application rates in the U.S. domestic fleet or for understanding how frequently equipment rotate into domestic routes following insecticide treatment. However, the World Health Organization (WHO) recommends several methods for treating aircraft with insecticide. Although there is evidence that these WHO guidelines may not always be followed, and that practices vary by airline, destination, and/or applicator company, the guidelines in combination with information related to other indoor environments provides a plausible basis for estimating insecticide loading rates on aircraft. The review also found that while measurements of exposure concentrations following simulated aerosol applications are available, measurements following residual treatment of aircraft or applications in domestic aircraft are lacking. Task 2 focused on developing an approach to monitor exposure concentrations in aircraft using a combination of active and passive sampling methods. An existing active sampling approach was intended to provide data immediately following treatment while a passive sampler was developed to provide wider coverage of the fleet over longer sampling periods. The passive sampler, based on a thin-film polymer-coated glass design, was developed specifically for deployment in the airliner ventilation system for long-term unattended monitoring of insecticide loading in the aircraft. Because access was not available for either treated aircraft or treatment records during the course of this study, the development and calibration of the passive samplers was halted prior to completion. Continued development of a field ready passive sampler for insecticides in aircraft would require collaboration with the airline industry to finalize the method for deployment and calibration conditions for the sampler. The Task 3 screening level modeling assessment used a dynamic two-box mass balance model that includes treated surfaces and air to explore the time-concentration history of insecticides in the cabin. The model was parameterized using information gathered during the literature review and run for several different insecticide use scenarios. Chemical degradation or sequestration in the surface compartment and mass transfer from the surface to the air limit the rate at which insecticides are removed from the system. This rate limiting process can result in an accumulation of insecticide in the airliner cabin following repeated applications. The extent of accumulation is a function of the overall persistence of the chemical in the system and the amount of chemical applied during each treatment.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

ACER	Air Transportation Center of Excellence for Airliner Cabin Environment Research
ACH	Air changes per hour
AER	Air exchange rate
ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers
AQIS	The Australian Quarantine and Inspection Services
CAS	Chemical Abstract Service
DCM	Dichloromethane
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
EVA	Ethylene vinyl acetate coating on POGs
FAA	U.S. Federal Aviation Authority
GC/MS	Gas chromatograph – mass spectrometer
IARC	World Health Organization International Agency for Research on Cancer
ICAO	The International Civil Aviation Organization
LBNL	Lawrence Berkeley National Laboratory
LOD	Limit of Detection for measurements
MQS	The New Zealand Quarantine Services
PAN	Pesticide Action Network
POG	Polymer coated glass sample cartridge
PUF	Polyurethane foam sample material
UCB	University of California, Berkeley
RED	U.S. EPA Re-registration Eligibility Decision for Permethrin
SVOC	Semi-volatile Organic Chemical
USDA	U.S. Department of Agriculture
USDOT	U.S. Department of Transportation
WHO	World Health Organization

This page intentionally blank

1.0 Introduction

Public Law 108-176 titled "Vision 100 – Century of Aviation Reauthorization Act" calls for a number of activities related to air quality in aircraft cabins. In response to Congressional directives, the Federal Aviation Administration (FAA) established the Air Transportation Center of Excellence for Airliner Cabin Environmental Research (ACER). Lawrence Berkeley National Laboratory (LBNL) was one of eight core institutions that originally made up the ACER. As part of ACER, and in response to language in Senate Report 108-146 (page 39) requiring the FAA Administrator to "collect pesticide exposure data to determine exposures of passengers and crew", LBNL undertook research that was initially aimed at measuring insecticide exposures on passenger aircraft.

However, LBNL was unable to gain access to treatment records or treated aircraft for the purpose of collecting exposure data during the course of this study. Therefore, the overall goal of the current project focused on developing sampling procedures and tools that, if implemented, could provide relevant measurements of on-board insecticide exposure for airline passengers and crew without impacting airline operation. Exposure concentration measurements in aircraft, along with knowledge of the treatment schedule of the aircraft, crew scheduling, and crew/passenger activity profiles, could provide a quantitative understanding of the link between insecticide use in aircraft and exposure levels experienced by occupants. Such exposure information provides a basis for assessing the health risk associated with various scenarios including long-term (chronic) exposure to a chemical through multiple exposure pathways and routes (aggregate), simultaneous exposure to multiple chemicals having common mechanisms of toxic action (cumulative), and short-term high-level exposures that may occur immediately following an application (acute).

The treatment of transport craft to prevent the movement of potentially invasive or disease-carrying insects, a process known as disinsection, began in the 1920s [1] and the practice was adopted in the United States and other countries by the late 1930s [2, 3]. The United States discontinued the routine spraying of aircraft in 1979 [1] but a number of countries still require disinsection and most countries reserve the right to treat planes should the need arise [4]. The risk of introducing West Nile virus to Hawaii by passenger aircraft was recently quantified [5] leading to a call for resumed residual disinsection of domestic aircraft [6]. This demonstrates that there is a real possibility that regulators will be faced with decisions about treating aircraft with some form of disinsection. There are clearly opposing views as to the efficacy and risks associated with chemical disinsection practices [1, 2, 7-11] so any decision to resume the practice on domestic flights, even though that option exists, is extremely difficult to make in the absence of scientifically defensible exposure and health effects data that is relevant to the aircraft cabin environment. A quantitative understanding of the source-to-dose linkage for insecticide use on aircraft could ultimately support an informed, risk-based decision about the safest means to prevent the spread of insect vectors via passenger aircraft.

This project is divided into three tasks. Task 1 includes a literature review to identify data gaps and provide key inputs needed to develop a sampling plan and support an initial modeling assessments for insecticides used in the aircraft cabin environment. Task 2 focuses on developing tools and procedures for collecting relevant insecticide concentration measurements in the airliner cabin. Task 3 includes preliminary modeling to explore the time-history of insecticide concentrations in the aircraft cabin.

A description of the individual tasks and results from this research are provided in the following sections.

2.0 A review of current insecticide application practices

The goal of this review is to provide a brief history of insecticide use on aircraft and to identify values for key inputs that are needed to evaluate insecticide exposures. We focus on identifying the most likely insecticides used to treat aircraft along with application methods, application rates and treatment frequency. In addition, we summarize physiochemical properties of insecticides that are used on aircraft along with environmental factors in the aircraft cabin that can influence the time history concentrations. Finally, we summarize existing data on exposure concentrations in the airline cabin following insecticide treatments and identify important data gaps in the characterization of insecticide exposure levels experienced by passengers and crew.

2.1. Insecticides used on passenger aircraft

A keyword search on the Pesticide Action Network (PAN) pesticides database (http://pesticideinfo.org/) for insecticides that are currently registered in the U.S. for use on aircraft returns 570 products. Searching for parent product[1] only reduces the number of actively registered insecticides for aircraft to 210. Narrowing the search further to insecticides categorized by specific chemical classes, found pyrethroids as the active ingredient in 120 products, n-methyl carbamate in 3 products, pyrazole in 7 products, chloro-nicotinyl in 2 products and "unclassified" for 75 products. Of the 75 products that listed "unclassified" as the chemical class of the active ingredient, most contain pyrethrins and pyrethroids. The active ingredients in the PAN database that are currently registered by the EPA for use on aircraft are listed in Table 1 along with physiochemical properties.

Because there is an absence of published data on the use of insecticides in passenger aircraft, and industry records are not available, it is not possible to know which chemicals are actually used in the domestic fleet and in what amounts. However, the WHO currently recommends only four active ingredients for disinsection – resmethrin, bioresmethrin, d-phenothrin and permethrin (cis/trans ration 25/75) [7]. The International Civil Aviation Organization (ICAO) surveyed member states regarding current practice for aircraft disinsection and found that of the 64 states responding to the survey, 37 required some form of disinsection and nearly all of those use the WHO recommended active ingredients d-phenothrin and permethrin although some of the other pyrethroids are also reported as being used (e.g., resmethrin, deltamethrin, cypermethrin) [8]. The New Zealand and Australian Quarantine Services require incoming aircraft to be treated with phenothrin and/or permethrin [9] but a draft guidance document for applying residual insecticide on aircraft in the United Kingdom recommends using deltamethrin [10, 11].

[1] The same parent product can be registered under many different brand names.

Table 1 Chemicals registered by the EPA for use in aircraft

Name	*CAS*	*MW g/mol*	*VP Pa*	*S mol/m3*	*log Kow*	*H mol $m^{-3}Pa^{-1}$*	*Log Koa*
prallethrin	23031-36-9	300	3.57E-03	2.67E-02	4.49	1.34E-01	8.76
allethrin	28434-00-6	302	1.60E-04	1.52E-02	4.78	1.05E-02	10.15
tetramethrin	7696-12-0	331	9.44E-04	5.53E-03	4.73	1.71E-01	8.89
resmethrin	10453-86-8	338	1.87E-02	8.88E-04	6.14	2.10E+01	8.21
phenothrin	26046-85-5	350	1.91E-05	2.77E-05	7.54	6.88E-01	11.10
permethrin	52645-53-1	391	2.91E-06	1.53E-05	6.50	1.89E-01	10.62
cypermethrin - beta	65731-84-2	416	2.31E-05	9.62E-06	6.00	2.40E+00	9.01
esfenvalerate	66230-04-4	419	2.00E-07	4.77E-06	6.20	4.19E-02	10.97
bifenthrin	82657-04-3	423	2.40E-05	2.36E-04	8.15	1.02E-01	12.54
cyfluthrin	68359-37-5	434	2.00E-08	6.91E-06	5.95	2.89E-03	11.88
cyhalothrin	91465-08-6	450	2.00E-07	1.11E-05	7.00	1.80E-02	12.14
deltamethrin	52918-63-5	502	2.00E-06	3.98E-07	6.20	5.02E+00	8.89

CAS – Chemical Abstract Service Registry number; MW – molecular weight; VP – vapor pressure; Kow – octanol/water partition coefficient; H – Henry's law constant; Koa – octanol/air partition coefficient. MW, VP, S, and logKow are taken from the EPA EpiWin software version 3.11. H is calculated as VP/S and logKoa is calculated as Kow*R*T/H where R is the gas constant (8.314 Pa*m3/mol/K) and T is the temperature (298.15 K)

Based on available international guidance the most likely active ingredients to be used on aircraft that are flying routes that require disinsection include permethrin and phenothrin. A survey of the PAN database suggests that other pyrethroids may be used on aircraft although no insecticides are registered in the U.S. for use in occupied aircraft cabins. Unfortunately we were not able to identify what specific insecticides are used on domestic routes and in what amounts but the findings suggest that pyrethroids, including permethrin and phenothrin, are the most likely insecticide used in aircraft.

2.2. Application rates of insecticide on passenger aircraft

As indicated above, there are a number of insecticides registered for use in domestic aircraft although the EPA does not register any aerosolized insecticide for use in the occupied aircraft cabin [10, 11, 16]. Although data are extremely limited regarding pest management practices on domestic aircraft, there is evidence that insecticides can be measured in the aircraft cabin on domestic planes. A recent study found quantifiable levels of insecticide (permethrin) in the cabin air on two of four domestic flights where semi-volatile organic compounds (SVOCs) were monitored [12]. No other insecticides were monitored on these flights and no information was available about whether the aircraft was treated domestically for general pest control or treated to comply with foreign quarantine regulations then rotated into the domestic fleet. Other than instructions on individual product labels, there is no publicly available guidance or information regarding application methods, amounts or frequencies for insecticides use in domestic aircraft [13].

The link between insecticide use and exposure cannot be quantified without knowledge of the chemical application rate even if measurements of concentrations on aircraft are available. The airline industry is not required to make their pest management records publicly available. In the absence of published records of insecticide use in passenger aircraft, in particular those used for domestic insect control, typical application rates in other indoor environments and/or application

rates on aircraft requiring disinsection to satisfy foreign quarantine regulations can provide a first approximation of plausible application rates and frequencies.

The EPA recently completed a Reregistration Eligibility Decision (RED) for Permethrin [14] in which extensive exposure and toxicological data were reviewed and summarized and a range of exposure scenarios were developed [18, 19]. Although the assessment supporting the RED did not consider permethrin use on aircraft, the results do provide residential exposure scenarios that consider post application surface residues. The indoor surface residues following use of a total release fogger containing 0.25% permethrin in a 2000 cubic foot space was 2.4 μg of active ingredient per cm^2. The typical broadcast spray using a 0.5% active ingredient (permethrin) mixture resulted in a surface residue of 15 $\mu g/cm^2$ and residential crack and crevice treatment resulted in a 7.5 $\mu g/cm^2$ residue. The RED also summarized a number of use patterns and maximum application rates subject to reregistration for indoor surfaces (commercial or domestic) treated with an emulsifiable concentrate formulation. The maximum application rate is listed as 0.7805 pounds per 1000 sq.ft or approximately 300 $\mu g/cm^2$. However, the application rate actually used in the RED assessment for indoor surfaces treated with spray was 0.0001 lb/sq.ft or approximately 40 $\mu g/cm^2$. Additionally, it was assumed that households treat approximately 5 times per year or about once every 9.5 weeks [14].

The New Zealand Quarantine Services (MQS) and Australian Quarantine and Inspection Services (AQIS) published guidelines for disinsection procedures [9] using permethrin and phenothrin. The Schedule of Aircraft Disinsection Procedures describe in some detail the method (based on guidance in the WHO International Health Regulations [7, 15, 16]) for treatment of aircraft flying into New Zealand and Australia. Specific quantities of insecticide are recommended for a range of different application methods and aircraft sizes but in general the target loading rate of active ingredient on surfaces of the aircraft cabin and cargo hold are 20 $\mu g/cm^2$ for all interior surfaces except floors where the target loading rate is 50 $\mu g/cm^2$. Treatment is required on an 8 week interval. A much higher concentration of the active ingredient is used in the emulsifiable concentrate for the disinsection procedure relative to that used in the EPA's RED document (i.e., 2% versus 0.5%). The higher concentration of active ingredient recommended by the quarantine services may be to reduce the amount of water used while applying the insecticide to surfaces in the aircraft. The procedure also recommends treatment of all surfaces in the aircraft cabin while the residential broadcast spray applications may be limited to the floors and wall areas around building penetrations.

Nevertheless, the recommended loading rates on indoor surfaces for permethrin are similar between the EPA's RED document that reviewed a wide range of commercial and residential indoor applications and the MQS/AQIS disinsection procedures where the application rates represent international recommendations for aircraft disinsection. Although it is unlikely that domestic passenger aircraft are treated at the same rate that is recommended for aircraft disinsection, in the absence of industry specific information on the domestic fleet, and in light of the use patterns for other indoor spaces as discussed in the EPA's RED document, an application or loading rate of 20-50 $\mu g/cm^2$ at 8 week intervals is selected to provide an upper bound treatment regiment for assessing exposure in aircraft cabins.

2.3. Application methods

The method of application for insecticides can influence exposure pathways where aerosols released to the air of occupied aircraft cabins can contribute to inhalation and dermal exposure while surface residues following treatment can contribute to dermal and non-dietary exposure (hand-to-mouth or object-to-mouth). There are no publicly available resources describing pest management practices in the domestic passenger airline industry so it is not possible to know exactly what methods are used by a given air carrier or on a given aircraft. Therefore, we rely almost entirely on internationally accepted guidelines to identify methods of application.

The WHO recommends four procedures for aircraft disinsection [7, 15, 16] depending on the destination country's preference. These procedures have been summarized in detail in a number of publications [1, 10, 11, 14, 22, 23]. The procedures can be classified as either aerosol delivered from spray cans or residual treatments using emulsifiable concentrates.

The aerosol treatments include "blocks away" where the aircraft cabin is sprayed after passengers have boarded and just prior to departure, "top of descent" where the cabin is sprayed in flight by flight attendants as the aircraft starts its descent and "on arrival" where the cabin is sprayed just prior to disembarkation of the passengers. These three aerosol treatments typically require a 2% phenothrin spray with an application rate of 10 grams of formulation per 1000 cubic feet of aircraft cabin or 7 mg of active ingredient per m^3 treated space. Assuming 100% of the active ingredient settles to the surface (ventilation system off) and the surface to volume ratio in the cabin environment is approximately 2.5 m^2/m^3 this equates to a surface loading of 0.3 $\mu g/cm^2$ per treatment. Another aerosol treatment is also available (not yet approved by the WHO) where the aircraft is treated prior to boarding or "pre-embarkation" [1, 23, 24] using a combination of 2% phenothrin and 2% permethrin in an aerosol spray where the phenothrin is a strong knock-down treatment and the permethrin provides some residual protection and acts as a repellant for insects. The surface loading for the pre-embarkation treatment for each insecticide would be approximately 0.3 $\mu g/cm^2$ per treatment.

The residual treatment method uses an emulsifiable concentrate with 2% permethrin with a target application rate of 20 $\mu g/cm^2$ on all interior surfaces (excluding windows and mirrors) except floors where a target loading rate of 50 $\mu g/cm^2$ is specified. Residual treatments are repeated on about an 8 week interval as indicated above and touchup applications are used between treatments as needed. There are other application methods for aircraft in the domestic fleet that may include spot treatment, fogging, bug bombs, crack and crevice treatment and traps [13] but documentation on these methods are not publicly available. There also is no publicly available information on the frequency that one or a combination of the treatment procedures described above are used on a particular aircraft so estimating the actual loading rate is not possible without access to treatment records. However, if we assume that an aircraft is treated with one of the aerosol treatments each day for 8 weeks the loading rate of insecticide would be comparable to a single residual treatment.

Although insecticides are not registered in the U.S. for use as disinsectants in occupied aircraft cabins, it is possible to estimate a plausible application rate and frequency by considering internationally recognized guidelines for residual disinsection treatments and aerosol disinsection treatments, in combination with domestic indoor broadcast treatments in residences and commercial establishments. These sources of information indicate a typical permethrin surface loading in the range of 20 $\mu g/cm^2$ to 50 $\mu g/cm^2$ at eight to ten week intervals. For an indoor

environment with a surface to volume ratio of approximately 2.5 m^2/m^3 this represents a continuous source term on the order of 10 to 20 mg/m^3/day.

2.4. Measured post-application concentrations

Although aerosol insecticide application in occupied aircraft cabins are not approved for use in the U.S., some domestic carriers fly to regions requiring disinsection, thereby exposing crew and passengers. In addition, most international governments including the U.S. reserve the right to use disinsection should the need arise [4]. Therefore, it is important to understand the source-to-exposure linkage for aerosol applications as well as for the residual or spot treatments that are more likely to occur in the domestic fleet. Two studies provide data on the short-term exposure concentrations following simulated in-flight aerosol treatments [17, 18]. The treatments in these papers were applied as "top-of-descent" applications and the concentrations in air (collected on glass fiber filters in the first study and filters backed with polyurethane foam in second) and loadings on several surfaces throughout the aircraft were measured.

The results are summarized in Table 2 for the air concentrations integrated over 40 minutes during and following the application. The active ingredient in these studies were natural pyrethrins in the first study and d-phenothrin in the second. The resulting concentration is normalized to the mass of active ingredient applied and the results are presented in the last column of Table 2. The fresh air exchange rate in the cabin was 22.2 per hour for all experiments except E3 where the air conditioning system failed during the application.

The results in Table 2 indicated that an aerosol application in an aircraft with cabin volume of 244 m^3 leads to a concentration in the cabin air (with air conditioning operating) of 63 ± 39 $\mu g/m^3$ per gram of insecticide applied and integrated over 40 minutes including the time of spraying. During one experiment (E3 in [18]) the researchers measured air concentrations during spraying and up to 5 minutes after then from 5 to 20 minutes and again from 20 to 40 minutes and found that the concentrations in the cabin air decreased rapidly (air concentration reduced to 0.1% of the initial concentration in about 0.3 hours) with air conditioning system operating. The data indicate an overall clearance half-life for removal of phenothrin from air when applied in aerosol spray in the airliner cabin with air conditioning packs operating (ACH = 22.2) is on the order of minutes (2.7 ± 0.3 minutes). As a result, most of the mass in the samples reported in Table 2 was collected in the first 10 minutes after spraying indicating that the short-term exposure concentration experienced from active spraying of aerosol in the aircraft cabin is likely more than 4 times the values listed in Table 2 with duration of the elevated exposure concentration less than 10 minutes (during and after spraying).

Table 2 Measured air concentrations in aircraft following aerosol application

Experiment Number	volume applied (g)	mass fraction active ingredient in formulation	mass active ingredient applied (g)	Air Conc. ug/m^3	Air Conc. normalized to application ug/m^3/g
1	107	0.003125	0.33	11	32.90
2	200	0.003125	0.63	40	64.00
3 (AC failed)	168	0.003125	0.53	65	123.81
4	176	0.003125	0.55	19	34.55
5	204	0.003125	0.64	21	32.94
6	170	0.003125	0.53	20	37.65
7	113	0.02	2.26	133	58.85
8	91	0.02	1.82	224	123.08

The first 6 experiments (1 – 6) were reported for pyrethrin applications in [17] and the last two (7 & 8) were reported for phenothrin applications as experiments 4 and 5 in [18]

Surface loading following aerosol treatment were also measured on several surfaces including folding tables (vertical), floor under seats, on seats, on headrests and in overhead bins (closed). Surface loading measured on tables and in overhead bins were several orders of magnitude lower than the other surfaces so are not repeated here. The results from the three fabric surfaces are summarized in Table 3. The surface loading is reported as both the measured value (ng/cm^2) and the loading normalized to the mass of active ingredient applied in the cabin (ng/cm^2/g). The second study [18] found higher loadings than the first [17] despite the similar application procedures and aircraft used. The main difference between the studies was the active ingredient measured and the type of aerosol formulation (size distribution) used in the application.

Table 3 Measured surface loading following aerosol treatment

Location	under seats		on seats		on headrests	
Experiment number	ng/cm^2	ng/cm^2/g	ng/cm^2	ng/cm^2/g	ng/cm^2	ng/cm^2/g
1	15	43	46	138	21	63
2	32	50	39	62	38	60
3 (AC failed)	36	68	56	106	52	99
4	9	15	12	22	20	36
5	26	40	46	71	34	53
6	29	54	42	78	35	66
7	262	116	714	316	1005	445
8	219	120	545	299	425	234

The measured surface loading for each location are given as mass per unit surface area (ng/cm^2) and mass per unit surface area per gram of aerosol applied in the cabin (ng/cm^2/g).

Based on the results in Table 3, the measured loading rate for surfaces from the two studies was approximately 100 ng/cm^2 per gram of active ingredient applied (average of all surface measurements in Table 3, standard deviation ~ 100). To relate this to a loading during a disinsection treatment we assuming an application rate of 0.2 g per 28.3 m^3 (WHO recommended rate [9, 19]), and a cabin volume of 244 m^3 (aircraft used in [17, 18]), which leads to 1.7 grams of active ingredient per application. A 1.7 gram application would result in a surface loading (with air conditioning packs on) of approximately 0.17 ug/cm^2. This is somewhat less than the expected

loading (0.3 ug/cm^2) that we calculated from a standard aerosol treatment (see Section 4.3) assuming an application rate of 10 grams active ingredients per 100 cubic feet of cabin space, 100% of applied insecticide settles to a surface and the surface to volume ration in an aircraft cabin is on the order of 2.5 m^2/m^3. This indicates that some of the active ingredient in the aerosol treatment is removed from the cabin by ventilation and either deposited in the recirculation ductwork or exhausted from the aircraft.

Measured concentrations following residual treatments are absent in the published literature. Unpublished data from samples collected on aircraft flying to a location requiring disinsection (Australia) have been summarized [20, 21]. The samples were collected by airline health and safety staff and, in some cases, by a flight attendant. Surface wipes and air samples were collected on aircraft that received residual treatment. The surface samples included wipes (smooth surfaces) and pieces of fabric and materials collected from the aircraft cabin and crew quarters. The results for "surfaces, fabrics and materials" had a median loading of 160 ng/cm^2 which is similar to what was found with the aerosol treatments described above. However, the range of concentrations or loadings found in the 91 samples was from 1.5 ng/cm^2 to 3.6 mg/cm^2 where the highest value was reportedly a sample of a puddle or residue formed during treatment. Air concentration measurements ranged from 2.2 to 1040 μg/m^3 for samples collect following treatment and below the limit of detection (<150 ng/m^3) for samples collected more than three hours post disinsection.

The only data available for domestic flights are from four flight segments that were monitored as part of ASHRAE Project 1262-TRP [12]. At least one isomer of permethrin was detected on two of the four domestic flights tested at levels of 0.9 ng/m^3 (cis-permethrin) and 1.1 ng/m^3 to 2.0 ng/m^3 (trans-permethrin) where the experimental limit of detection (LOD) for this study was 0.8 to 0.99 ng/m^3. The lack of detectable values from the industry study was likely due to the higher LOD (150 ng/m^3) relative to the ASHRAE project.

Overall, this review indicates that there are sufficient measurements from aerosol treatments to estimate loadings and exposure concentrations during and immediately after an aerosol application but data for aircraft treated with regular residual disinsection or periodic treatments for infestations is not sufficient to estimate exposure concentrations with any confidence. Measurements of concentrations in air, suspended aerosols, settled dust and surface loadings should be collected on aircraft with known insecticide applications histories before representative exposure scenarios for passengers and crew can be developed.

2.5. Health effects of insecticide use on aircraft

Pyrethroids entered the marketplace in the 1980s and rapidly increased in market share because they seem to have remarkable knockdown properties for insects while at the same time having a very low mammalian toxicity. The low toxicity is primarily due to efficient and rapid enzymatic degradation [12, 26, 27]. Although the compounds are metabolized and excreted rapidly in mammals, their widespread use has resulted in a number of reported neurological responses and transient skin irritation from high exposures [22, 23]. The primary target organ for type I pyrethroids such as phenothrin and permethrin is the nervous system [14]. However, the World Health Organization considered a large number of reviews including those by the International Programme on Chemical Safety, the Expert Committee on Vector Biology and Control and the International Agency for Research on Cancer, and concluded that currently used preparations for disinsection, i.e., permethrin and phenothrin, were safe if used correctly. A critical conclusion

from their recent review of disinsection [7] was that "given the understanding of the mode of action of pyrethroids and low exposure from aircraft disinsection it is unlikely that this procedure will precipitate or influence any pre-existing disease of passengers and crew." Whether exposures are in fact as low as indicated by the WHO report still remains to be demonstrated and understanding of the toxicity of this highly used class of chemicals continues to evolve.

The literature is clear that the unintended transport of insects on aircraft presents a risk to public health and the environment [1, 2, 5, 9, 12, 28-30] and most agree that there is a serious need to control the transport of insects in order to prevent the movement of disease vectors and environmentally important invasive species. The use of insecticide treatments or chemical disinsection procedures mainly using pyrethroids has been the preferred and recommended practice in the airline industry primarily because of the cost, efficacy, ease of use and low human toxicity. Those arguing in favor of chemical disinsection practices generally have concluded that although there are anecdotal reports of toxicity related to insecticide treatment in aircraft, there have been no published reports linking insecticide use in aircraft to an adverse effect in airline crew or passengers [1, 8, 12, 24]. Studies have been published that found pyrethroid use on aircraft poses a hazard for flight crew [21, 24]. However, these studies were both retrospective so a direct cause/effect relationship could not be established.

Despite the fact that pyrethroids are heavily used in a wide range of applications and there are few published observations of serious adverse effects, there are still a number of very important data gaps in our knowledge about the toxicity of pyrethroids [25, 26]. Of particular interest, or concern, is the potential for developmental neurtoxicity [25] and reproductive toxicity highlighting the need to quantify the routes and potential magnitude of exposure for individuals traveling or working on treated aircraft. Although the World Health Organization International Agency for Research on Cancer (IARC) has concluded that several pyrethroids including permethrin are "not classifiable" as to carcinogenicity [26], the EPA recently classified permethrin as "Likely to be Carcinogenic to Humans" with a potency value (Q_1*) of 9.6×10^{-3} $(mg/kg/d)^{-1}$ [14, 26].

This review found that although there is agreement regarding the need to control the unintended transport of insects on aircraft, there are clearly opposing views as to the efficacy and risks associated with chemical disinsection practices [1, 2, 7-11]. Unfortunately, there have been no systematic studies to confirm or refute the possible links between insecticide use on aircraft and adverse effects experienced by passengers and/or crew. Understanding risks associated with any chemical use requires knowledge of both toxicity and exposure. Our understanding of the toxicity of pyrethroids continues to evolve and will likely require a periodic re-assessment of the different applications given knowledge about exposures. What is unique to the application of pyrethroids on aircraft is that knowledge about exposure is almost completely lacking. A large number of pyrethroid applications have been studied to characterize potential exposure [35-42] but only a few studies have considered applications on aircraft [17, 18] and these are focused on a single application method (aerosol disinsection). Information on residual treatment or treatments used in the domestic fleet are completely lacking.

3.0 Scoping measurements of insecticides on aircraft

The review of current insecticide application practices revealed that limited measurements linking insecticide applications on aircraft to exposure concentrations were available for aerosol

treatments. However, measurements were completely lacking for residual or episodic treatment on domestic aircraft. Therefore, the second task of this project was to explore options and identify appropriate methods for characterizing the distribution of exposure concentrations on treated aircraft with the main focus being on the domestic fleet but also on domestic airlines (and crew) flying to countries requiring disinsection. The ultimate goal is to provide tools and data that will help characterize the link between chemical use and exposure on aircraft. Measurements of exposure concentrations representing the different potential routes of exposure (e.g., inhalation, dermal, ingestion) at different time intervals following known applications are necessary to determine intake and to assess the risks associated with a particular use of a chemical. This information is also needed if the assessment is to be extended to different uses and exposure scenarios on aircraft. In short, there remains a need for source-to-exposure relationships for insecticides released in or applied to passenger aircraft.

With the focus on domestic flights where insecticide application records are not available, we anticipated the need for a large number of samples to identify and/or develop appropriate models for estimating the distributions of exposures. The large number of samples would be needed to establish trends in exposure concentrations where insecticide applications may be episodic and highly variable. We would need enough samples to reconstruct plausible insecticide application times and amounts given the significant uncertainty (and variability) associated with integrated pest management practices (including but not limited to disinsection) across the industry. It is also important to determine activity patterns of passengers and crew that result in contact with exposure media or residues in treated aircraft but the initial focus of this work is on establishing exposure concentrations.

The insecticides that are used and/or registered for use on aircraft can be classified as semi-volatile organic compounds (SVOCs) because of their low vapor pressure and high lipid solubility as indicated by their elevated octanol water partition coefficients. Only trace amounts of these chemicals can typically be found in the gas phase after aerosols from initial treatment has dissipated but gas-phase measurements can still provide an important indication of surface loadings in a contaminated space [27]. In addition, although most of the mass of these chemicals will be sorbed to surfaces, dust and suspended aerosols [44-46], indoor air is thought to be an important transport pathway for mixing and/or removing these bound residues and there is evidence that the air interacts rapidly with surfaces providing an in integrated measure of the chemical loading, or fugacity[2] in the space. There is evidence that a chemical's fugacity is a good indicator of exposure for individuals in a particular space [28]. Therefore, measured air concentrations can provide a marker of the presence of these insecticides in the indoor environment and a metric for estimating intake by inhalation and non-dietary ingestion (saliva). But surface measurements are also needed to characterize the distribution of insecticide in the cabin and estimate intake by dermal and other non-dietary pathways (e.g., hand-to-mouth and object-to-mouth).

To identify sampling methods for characterizing the distribution of exposure concentrations for insecticides (and other toxic chemicals) in passenger aircraft we investigated the use of surface

[2] Fugacity is related to a substances chemical potential but has units of pressure and unlike chemical potential is linearly related to concentration in a media which provides a convenient state variable for mass balance modeling. The gradient of fugacity across two adjacent media (air/carpet) also provides an indication of the direction of mass flow in the system because a substance always diffuses from areas of high fugacity to areas of lower fugacity. When fugacity is equal in two adjacent compartments then the concentrations are in equilibrium.

wipes (hard surfaces), surface vacuum (soft surfaces and fabrics), active air sampling (short-term), passive air sampling (long-term integrated), and urinary biomarkers as surrogates and indicators for the different possible exposure pathways.

Active air sampling methods that draw air through filters and sorbent material are readily available for pyrethroids [29] and at least one approach has been demonstrated on aircraft in flight [12]. Therefore, no further development of active air sampling methods were included in this study. Surface sampling methods are critical for understanding exposure pathways. The development of surface sampling methods has been undertaken by ACER team members at the University of Medicine and Dentistry of New Jersey so work on surface sampling was not conducted at LBNL. After assessing the various sampling techniques, the work conducted at LBNL focused on the development of a sampling method that could provide an integrated measure of air concentrations over extended periods in a large number of aircraft with minimum cost and impact on the operation of the aircraft. These samplers are intended to screen a large number of aircraft in the absence of information identifying which aircraft might have been treated with insecticides. The passive samplers are also expected to be useful for augmenting active sampling and surface sampling in specific aircraft. The work related to passive sampler development for aircraft is described in the following sections.

3.1. Rational for passive sampling of SVOCs on aircraft

A large number of aircraft need to be sampled to provide a statistically representative distribution of exposures. This is particularly true for observational studies that lack information about timing and amount of insecticide treatments on specific aircraft. Active sampling techniques provide a measurement that is integrated over the duration of a single flight segment at a single location in the aircraft cabin and the sampling apparatus must be accompanied on each flight by a technician. Passive sampling could be deployed unattended and remain on the aircraft for extended periods. If deployed in a well mixed area such as the return air channels in the cheek of the aircraft, fore and aft of the recirculation manifolds, then these samples could “see” the entire cabin atmosphere providing an integrated measure with only a small number of unattended samplers. Because passive samplers do not require pumps and flow controllers they can be deployed in places where active sampling apparatus are not feasible.

Discussions among the ACER members and with industry representatives indicated that access to aircraft for the purpose of measuring insecticide levels would be difficult. Therefore, it was important that the final sampling method be simple, inexpensive to operate, robust (i.e., not easy to break) and reliable. In addition, the sampler must not be overly intrusive to the operation of the aircraft, to the performance of the flight attendants and crew and to passengers on the aircraft. Passive samplers that are deployed and then later retrieved by a technician during the overnight layover period for an aircraft seems to satisfy the need for simplicity and minimal impact on airliner operations and crew.

Recent advances in the development and calibration of passive air samplers for SVOCs has demonstrated their capability to measure air concentrations for SVOCs [30] providing an opportunity for deploying a large number of samplers on aircraft in the domestic fleet. Monitoring aircraft with passive sampling technology can provide much greater coverage (temporally and spatially across multiple aircraft) with much less effort/expense as compared to the coverage that can be achieved with active samplers.

3.2. Selection of passive sampler design for SVOCs

A number of passive sampling technologies have been developed for sampling SVOCs in air as indicated in the recent review by Namiesnik et.al, [30]. The passive samplers differ primarily in the type of sorbent material used which influences the capacity of the sampler and the uptake rate during sampling. Typical samplers include polyurethane foam (PUF) disks, triolein-filled low density polyethylene tubes and thin-film polymer coated glass (POG). The uptake profile for passive samplers include three distinct phases including 1) the linear region when uptake is a function of only the mass transfer rate, the projected surface area of the air/sorbent interface and the concentration in the air, 2) a curvilinear phase where the concentration in the sorbent reaches a point where feedbacks result in a reduction in the net uptake rate, and 3) an equilibrium phase when no more net uptake occurs and the mass in the sorbent is a function of the air/sorbent partition coefficient [31]. The ideal region for a passive sampler to operate is in the linear region.

Polymer coated glass samplers are generally considered rapidly equilibrating but for the compounds of interest to this work with log K_{oa} values in the range of 10-11, the sampler is expected to remain in the linear range for several to tens of days depending on the volume of polymer coating and the interfacial surface area [50-52]. The polymer coated glass samplers are also quite robust and easy to prepare and handle prior to use then easy to extract after use. The polymer coated glass was therefore selected as the basis for the prototype samplers to be used in aircraft.

Prior to development of the prototype sampler, researchers visited an aircraft manufacturer to discuss cabin air flow and ventilation characteristics [32, 33] and to identifying potential locations to deploy the samplers. The visit included a walkthrough of several aircraft. Based on the characteristics of the passive sampler and the cabin air flow, we identified the return air stream in the cheeks of the aircraft as a potential sampling location. This location was selected because it integrates the air flow from return air in the cabin either fore or aft of the wing box. Placing a sampler in the cheek just aft of the wing box or near the intake to the mixing manifold where the return air is collected was expected to provide the most representative measure of the average cabin air, assuming the aircraft did not have an overhead air recirculation system. This visit provided an indication of the size and shape of the sampler but an actual location for deployment was not identified on this trip.

3.3. Development of passive sampler prototype for SVOCs

The polymer-coated glass samplers that are described in the literature were prepared using glass tube sections installed in stainless steal housings [49-52, 55]. The design was not practical for deployment in aircraft because of its size and shape. To prepare a more compact sampler while maintaining the capacity (i.e., volume of sorbent) we elected to start with segments of glass honeycomb denuder housed in aluminum containers (Figure 1) that could be hung from or attached to various locations in the aircraft. The final design of the housing for the samplers would depend on mounting location but the simple aluminum housing sleeve was selected as a preliminary design. Ten prototype samplers were constructed for initial testing.

Figure 1 Prototype polymer coated glass (POG) passive sampler and aluminum housing

A method was developed to apply the polymer coating on the denuder segment by dipping the segment into a solution of ethylene vinyl acetate (EVA) dissolved in dichloromethane [34]. In summary, the clean glass sampler is dipped into a 2% solution of EVA to produce a uniform polymer film on all the glass surfaces of the sampler. A 5 mm space at the top of the sampler is left uncoated to provide a controlled diffusion boundary layer. The depth of this diffusion pathway could be modified to increase or decrease the uptake rate into the sampler depending on need. The coated sampler was installed in the aluminum holder and held in place with retaining clips to keep the sampler firmly in place and with Teflon o-rings to prevent the segment from moving side-to-side.

To ascertain the uniformity of the polymer coating, we coated several samplers then recovered and isolated the polymer layer. We found a 10% variance in the amount of polymer recovered with an average recovery of 440 mg. This was higher than previous studies using a single glass tube sampler where polymer mass was on the order of 10-15 mg/sampler indicating either a thicker film on the denuder segment or a larger surface area. A thinner film could be achieved, if necessary, using a more dilute starting solution of EVA.

We also determined recovery of the analyte from the polymer. The polymer is extracted from the glass segment with 3 consecutive dichloromethane (DCM) washes. The polymer is separated from the analyte by solvent exchanging to hexane, followed by precipitation of the polymer by rapid change in the solvent polarity which is achieved by adding methanol. After the EVA is precipitated it is removed from solution by centrifuge and the analyte remains in the supernatant, which is decanted and solvent exchanged back to DCM. Because we needed to use active sampling to calibrate the passive samplers, polyurethane sample trains were also developed. Analyte recovery experiments were conducted using both PUF and POG samplers. In each case

both d-phenothrin and mixture of cis- and trans-permethrin was spiked into each sampler type. The recovery levels of each insecticide were measured using an ion trap GC/MS and the results are summarized in Table 4. In the PUF sampler, 1000 ng of each insecticide was used while in the POG sampler, 100 ng of each insecticide was used.

Table 4 Recovery results for phenothrin and permethrin spiked on PUF and POG samplers

Sampler Type	*phenothrin*		*cis and trans- permethrin*	
	average	CV	average	CV
PUF (n = 3)	85%	26%	48%	6%
POG (n = 6)	113%	25%	86%	48%

All extracts were analyzed on a Varian 4000 GC/MS. A 2 μL injection volume was introduced into the type 1177 inlet splitless mode with a pressure pulse of 40 psi lasting 0.75 minutes. The inlet, transfer line, manifold and trap temperatures were 250 °C, 270 °C, 50 °C and 180 °C, respectively. The constant flow mode (0.9 ml/min Helium) was used with a starting oven temperature of 150 °C held for 1 minute then ramped to 280 °C at 10 °C/min holding for 2 minutes then ramping to 300 °C at 25 °C/min with a final hold time of 5 minutes. A 10 m Rapid-MS fused silica column with inside diameter 0.53 mm and film thickness 0.25μm (FactorFour, Varian) was used for separation of analytes. The mass spectrometer was run in internal electron ionization mode and data was acquired in full scan mode. A linear calibration curve was created from pure standards of phenothrin and permethrin (cis/trans 25/75) (Sigma Aldrich, Riedel-de Haen) spanning a range from 10 pg to 1000 pg and ^{13}C labeled cis-permethrin (Cambridge Isotopes) was used as a recovery standard and ^{13}C labeled trans-permethrin (Cambridge Isotopes) was used as an internal standard.

3.4. Calibration of passive sampler prototype for SVOCs

The theory for uptake of SVOCs from air into a thin-film passive sampler has been described [35]. The net rate of accumulation in the film is

$$V_{EVA}\left(dC_{EVA}/dt\right) = k_A A_{EVA}\left(C_A - C_{EVA}/K_{EVA-A}\right) \qquad \text{Eq. 1}$$

where V_{EVA} is the volume of ethyl vinyl acetate (EVA) film on the glass cartridge (cm^3); C_{EVA} is the concentration of target chemical in the film (ng/cm^3), k_A is the air-side mass transfer coefficient (cm/d); A_{EVA} is the interfacial area between air and film (cm^2), C_A is assumed to be a constant air concentration but in practice is the average concentration over the sampling period (ng/cm^3); and $K_{EVA\text{-}A}$ is the EVA-air partition coefficient. The EVA-air partition coefficient has been shown to be related to the octanol-air partition coefficient as

$$\log K_{EVA-A} = (1.148 \pm 0.096)\log K_{oa} - (1.136 \pm 0.82) \qquad \text{Eq. 2}$$

Because K_{oa} is very large ($\log K_{oa} > 10$) for the insecticides that are used on aircraft and the concentration in the film is small during the initial phase of uptake, equation 1 reduces to

$$\left(dC_{EVA}/dt\right) = \left(\frac{k_A A_{EVA}}{V_{EVA}}\right) C_A \qquad \text{Eq. 3}$$

Equation 3 is the relationship that is used to calibrate the sampler for a given effective film thickness (V_{EVA}/A_{EVA}) by deploying the sampler in a system with a known and constant air concentration and plotting the uptake rate in the sampler film versus time. This calibration process is also used to evaluate the linear range of the sampler which is important for determining the length of time that the sampler can be deployed for a single sampling event.

The diffusion path length in the passive samplers can be adjusted by changing the depth into the honeycomb denuder cartridge where the polymer coating starts and/or the depth inside the housing where the polymer coated denuder segment is mounted. This is important to minimize the effect of variations in airflow on sampling rate, particularly if the sampler is going to be deployed on aircraft over multiple days where air flows are expected to change during operation and overnight layover periods. The linear range of the sampler can also be adjusted if necessary by adjusting the effective film thickness.

A chamber was developed to calibrate the samplers. The chamber, based on a continuous stirred tank reactor design , is a cylindrical frame that is constructed with Teflon-coated aluminum that is wrapped in a transparent Teflon film (Fig. 2). The chamber has a volume of ~ 395 liters which is large enough to deploy several samplers simultaneously and small enough to allow the full air stream to be sampled if necessary for low concentration SVOC measurements. The continuous stirred design provided a well-mixed system that could be sampled from several different sampling ports if necessary. Chamber materials were selected to minimize the interaction of pollutants with the chamber walls. Outside air is introduced into the top of the chamber after being conditioned by passing through a pre-filter, activated carbon and high efficiency filter, chilled to a fixed dew point, reheated and then humidified to an RH representative or the airline environment using an ultrasonic humidifier on a rheostat control.

Switching valves and multiple sample ports are used in the chamber to provide continuous flow while collecting long-term integrated SVOC samples by diverting the full chamber flow through the SVOC sample cartridge or a bypass port during sample cartridge installations or changes. The chamber temperature is controlled by the room temperature and environmental variables (T, RH and internal pressure) are logged continuously during operation.

A source of phenothrin and permethrin was created by filling a 1 gallon steel can with small pieces of polyurethane foam. The pieces were soaked in a solution of phenothrin and cis- and trans-permethrin containing 100 mg of each. After the solvent evaporated, the can was sealed and placed in a 40 C oven. A nitrogen or dry air stream was introduced into the source can at flow rate of 1 liter per minute and transferred from the source can to the calibration chamber through a heated line. An alternate approach to providing a long-term steady state concentration in the chamber would be by adding treated materials directly to the chamber.

Figure 2 Chamber developed to calibrate passive samplers showing several samplers in the chamber along with a control (in can).

3.5. Current status of passive sampler prototype development

Before initiating the calibration process, a second trip was made to an airliner manufacturer to make a final selection of sampler deployment location(s) and to identify options for mounting the samplers. In addition, details on environment conditions in the deployment locations were sought in order to optimize the calibration conditions to represent expected field conditions. After touring aircraft and discussing options with airline manufacturer engineers it was determined that airline company engineers would need to participate in this final design stage for the housing/sampler and the selection and approval of both the deployment location and deployment method.

Several attempts were made by researchers to gain access to airline company engineers, to aircraft, and to the information that was needed to finalize the design and calibration conditions but these attempts were unsuccessful. Without industry participation we could not access information or the approval needed for the final sampler housing design, or acquire information to optimize the calibration conditions, so work on development of the passive samplers was halted.

4.0 Modeling the fate of insecticides on aircraft

In the absence of direct observations or measurements of insecticide exposures on aircraft, models provide a test bed for exploring the relationship between insecticide application rates and the time-history of exposure concentrations [36]. Although never more than an attempt to capture reality, a model can at least capture the most important aspects of the real system while excluding the nonessential details [37]. These simplified systems in models provide an opportunity to explore the behavior of more complicated systems in the absence of detailed measurements. The models can also provide a basis for developing sampling plans for collecting relevant measurements and, when observations become available, to help interpret the behavior of the system.

After the time-history of exposure concentrations is estimated and/or measured, and with adequate knowledge about the activity patterns of exposed individuals, exposure concentrations in the different media can be combined with contact rates and physiological parameters to estimate intake or potential dose. With knowledge of a chemical's toxicity, these dose estimates can be used to estimate risk of an adverse health outcome as a result of the given application and exposure scenario.

In this section, we focus primarily on the first step in this process, i.e., estimating the time-history of concentrations in the air and on surfaces for specific insecticide application scenarios in the airliner cabin. We approach this problem using a relatively simple dynamic box-model that represents the cabin environment.

4.1. Conceptual model formulation

We recognize that the composition of the indoor environment and the air handling systems in modern aircraft are not simple systems. The aircraft cabin environment includes a range of materials such as the fabric surfaces (carpet and seats), smooth surfaces (counters, windows, walls, ceiling and overhead bins), air, and a number of less obvious compartments such as organic film that builds up on impervious surfaces [38, 39], aerosols and dust that accumulate in the different compartments, and the individuals that actually occupy the cabin for a significant portion of time. All of these compartments and surfaces are potentially treated in an aircraft and certainly all interact with chemicals that are released to the cabin air. But to simplify the initial modeling we reduce the system to two primary well-mixed compartments that exchange mass across a shared interface. The two compartments include air and a generic surface as illustrated in Fig 3 along with the relevant mass transfer processes.

Both the air and surface compartments are assumed to have a constant volume and the chemical of interest is assumed to be well mixed in that volume. We define the volume of the air as 28.5 m^3 and the surface-to-volume ratio for fabric material in the cabin as 1.4 m^2/m^3 based on values reported for an existing simulated aircraft cabin that has been used extensively for cabin air quality research [40]. The volume of the surface compartment depends on the depth to which a chemical is expected to mix. Bennett and Furtaw [36] have selected representative values for "carpet", "vinyl" and "organic film" as 1×10^{-2} m, 5×10^{-4} m, and 1×10^{-7} m, respectively. Given the low vapor pressure and high lipid solubility of the insecticides used in aircraft, we do not expect the chemicals to migrate deep into the fabric layer so we specify an initial thickness of the surface as 1×10^{-4} m. The remaining parameters used to describe mass transport are described in the following section that describes the mathematical formulation.

By keeping track of gains and losses in each volume of the conceptual model illustrated in Fig. 3, we arrive at a mass balance for each of the two compartment volumes

$$\frac{dM_a}{dt} = J_a - D_{as} - P_{as} - R_a - A_a + D_{sa} + P_{sa} \qquad \text{Eq. 4}$$

$$\frac{dM_s}{dt} = J_s + D_{as} + P_{as} - D_{sa} - P_{sa} - R_s \qquad \text{Eq. 5}$$

where M_i are the inventories (mass) of chemical in the air (i = a) and surface (i = s) compartments; J_i is a direct and continuous source to each compartment; D_{ij} is the diffusive mass transfer from compartment "i" to compartment "j"; P_{ij} is the deposition and resuspension mass transfer of chemical sorbed to particles; R_a is loss by reaction in the air compartment and R_s is the overall loss by reaction, irreversible sequestration in the surface compartment and/or cleaning; and A_a is removal from the air compartment by ventilation and/or filtration.

Each of the process variables (J_i, D_{ij}, P_{ij} and A_i) can either be specified based on knowledge of the system or derived mathematically based on physiochemical and environmental properties. For example, the source terms in each equation (Eqs. 4 and 5) would typically be specified as part of the particular scenario that is being tested while the advection term in Eq. 4 (A_a) is the mass flux (mass/time) out of the system that occurs through cabin ventilation and is simply a function of the air exchange rate and the mass in the air compartment.

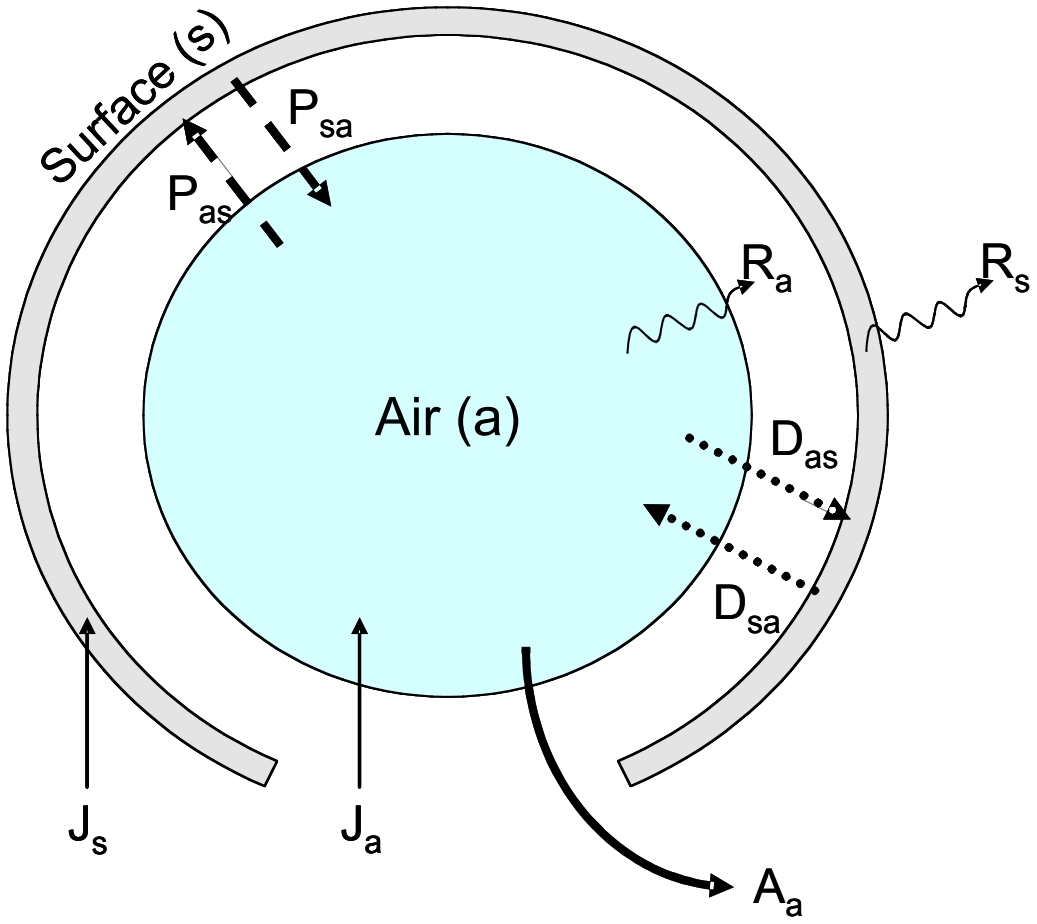

Figure 3 Conceptual 2-box model of the aircraft cabin environment showing the mass transfer processes affecting the time-history concentration in each compartment. These processes include a direct and continuous source, J_i to each compartment for air (i = a) and surface (i = s); particle deposition from air to surface, P_{as} and resuspension from surface to air, P_{sa}; diffusive mass transfer, D_{ij} where "i" is the source compartment and "j" is the receiving compartment; removal by reaction in air, R_a or by reaction and/or sequestration from surface, R_s; and advection out of the system through ventilation and/or filtration, A_a.

4.2. Mathematical model formulation and parameterization

Each of the processes listed in Eqs. 4 and 5 represent mass fluxes (mol/d) that are either introduced directly into the individual compartments, transferred across the shared interface between the two compartments, or removed from the individual compartments. We can specify these mass fluxes in terms of diffusion, advection or reaction processes and assuming a constant volume of each compartment we can derive equations for mass flux in terms of concentration.

The resulting mass balance for the conceptual model described above can be written as a system of first-order differential equations such that the time dependent concentration in the air compartment is

$$\frac{dC_a}{dt} = \frac{S_a}{V_a} - \left(R_a + \frac{f}{V_a} + \frac{U_{sa} A_{sa}}{V_a} + v_{da} K_{da} \rho_{da} \right) C_a + \left(\frac{U_{sa} A_{sa}}{K_{sa} V_a} + \frac{v_{dc} K_{dc} \rho_{dc} A_{sa}}{V_a} \right) C_s \qquad \text{Eq. 6}$$

and the time dependent concentration in the surface compartment is

$$\frac{dC_s}{dt} = \frac{S_s}{V_s} + \left(\frac{U_{sa} A_{sa}}{V_s} + \frac{v_{da} K_{da} \rho_{da} V_a}{V_s} \right) C_a - \left(R_s + \frac{U_{sa} A_{sa}}{K_{sa} V_s} + \frac{v_{ds} K_{ds} \rho_{ds} A_{sa}}{V_s} \right) C_s \qquad \text{Eq. 7}$$

The variables in Eqs. 6 and 7 are defined in Table 5 along with initial values used in the model with the chemical properties of permethrin used as an example. Each of the terms in parenthesis represent a different transport/transformation process and is given as a rate constant (1/d). Shaded cells in Table 5 indicate that the parameter is calculated from other properties in the table. If the parameter does not have a symbol associated with it, then that particular parameter is not used in the mass balance or in calculation of other parameters and is just provided for information.

The initial surface loading given in Table 5 or "starting surface concentration at t=0" represents a loading of 20 μg permethrin per square centimeter of surface compartment distributed evenly throughout the depth of the surface compartment. Continuous sources and initial concentrations in the air are also available in the mass balance and are used to explore the distribution of insecticide following a direct aerosol application to the air.

The physiochemical properties in Table 5 are chemical specific and are listed in Table 1. The Henry's law constant and the logarithm of the octanol/air partition coefficient (Log K_{oa}) can be estimated in the absence of measured values where $H=VP/S$ and $K_{oa} = K_{ow} \times R\_gas \times Temp/H$ where *R_gas* is the universal gas constant (Pa m^3 mol^{-1} K^{-1}), *Temp* is the average temperature in the system (K) and *H* is the Henry's law constant (mol m^{-3} Pa^{-1}).

The reaction rate constants in air and surfaces represent a removal of the chemical by degradation pathways and for surfaces can also include a sequestration pathway where the chemical either binds irreversibly to the surface material or migrates so deep into the surface that it is essentially removed from the system. Values for these rate constants and sequestration rates indoors are extremely limited. However, the reaction rates for insecticides indoors is generally slower than the reaction rates for comparable mechanisms outdoors [37, 39, 40] so, we assume as a general rule, that chemicals will tend to persist longer indoors than outdoors.

Table 5 Input parameters used in the dynamic 2-box air cabin model for insecticides

Description	Symbol	Value	Units
Chemical properties			
Chemical name		Permethrin	
Chemical CAS number		52645-53-1	
molecular weight	MW	391	g/mol
vapor pressure	VP	2.91E-06	Pa
water solubility	S	1.53E-05	mol/m^3
log (octanol/water partition coefficient)	log Kow	6.50	
Henry's law constant	H	1.89E-01	mol/m^3-Pa
log (octanol/air partition coefficient)	Log Koa	10.62	
Gas Constant	R_gas	8.314	Pa-m^3/mol-K
Temperature	Temp	298.15	K
reaction in air	R_1	0.00	d^{-1}
reaction in/on surface	R_2	0.00	d^{-1}
surface/air partition coefficient	Ksa	1.8 E+07	m^3/m^3
particle/air partition coefficient	Kda	2.1 E-02	$m^3/\mu g$
particle/carpet partition coefficient	Kds	1.2 E-09	$m^3/\mu g$
overall diffusive MTC velocity	Uas	5.0E+01	m/d
Environmental properties			
cabin volume	Vol_1	28.5	m^3
Surface to volume ratio	SAI	1.4	m^2/m^3
area of treated surface	Asa	39.9	m^2
Surface compartment thickness	del_S	1.00E-04	m
Volume of surface compartment	Vol_2	3.99E-03	m^3
air changes per hour	ACH	13.5	1/h
particle mass conc. in air	rho_da	10	$\mu g/m^3$
particle loading in surface	rho_ds	1.00E+01	$\mu g/m^2$
particle deposition rate coefficient	v_da	8.00E+00	1/d
particle re-suspension coefficient	v_ds	6.00E-05	1/d
particle deposition velocity		5.71E+00	m/d
particle re-suspension velocity		6.00E-09	m/d
Source terms and Initial values			
Continuous source to air at t=1	S_1	0.00E+00	$mol/d/m^3$
Continuous source to air at t=2	S_1b	0.00E+00	$mol/d/m^3$
Starting air concentration at t=1	C0_1	0.00E+00	mol/m^3
Starting surface concentration at t=1	C0_2	5.11E+00	mol/m^3
Continuous source to surface at t=1	S_2	0.00E+00	$mol/d/m^3$

Partition coefficients listed in Table 5 are calculated from physiochemical properties and/or regression analyses. The surface/air partition coefficient is based on the regression analysis for carpet without pad [36] and is given as K_{sa}=10^(3.82-0.62×LogVP) ($m^3_{(air)}/m^3_{(surface)}$). The partition coefficient for suspended particles [41, 42] in the air is given as a function of the chemical's lipid solubility and the organic composition in particles so that K_{da}= 10^(Log(K_{oa})+Log(f_{om})-11.91) ($m^3_{(air)}/\mu g_{(particle)}$) where f_{om} is the organic fraction in particles and we assume a value of 0.3 [36]. The partition coefficient between dust and carpet is the ratio the

particle/air and the air/surface partition coefficients such that $K_{ds}=K_{da}/K_{sa}$ ($m^3_{(surface)}/\mu g_{(particle)}$) assuming the particle composition is similar for particle in the air and surface compartment.

For chemicals with high lipid solubility and low vapor pressure, the total diffusive mass transfer across an interface between a surface and an air compartment is limited by the air-side mass transfer rate [43]. The air-side mass transfer can be estimated from the ratio of a chemical's diffusivity in air and the air-side boundary layer thickness over the surface. The diffusivity is a function of a chemical's size (or molecular weight) and for the insecticides of interest in Table 1 is on the order of 0.5 m^2/d . Typical values for the air-side boundary layer thickness range from 0.1 to 1 cm [37] so that a typical value for diffusive mass transfer is selected to be 50 m/d.

The environmental properties listed in Table 5 describe the size and composition of the compartments along with advection rates such as ventilation and particle transport. The volume and interfacial area have been described earlier. The fresh air exchange rate (AER) in aircraft can vary between 10 and 22 air changes per hour or ACH [17, 24, 25] when the air conditioning is active. The ACH is likely to be much lower when the equipment is idle during layovers. With doors closed this value could approach zero but we assume a value of 0.5 ACH during idle periods. Reported values for aircraft utilization indicate a range between ~ 5 and 15 hours per day [44] and ramp-to-ramp times add about 20% to that value. Therefore, we assume that a typical aircraft is actively ventilated for approximately 16 hours per day at 20 ACH with an 8 hour overnight layover at 0.5 ACH resulting in a long term average of 13.5 ACH.

Particle mass loading in air is likely to be low on aircraft but accumulation on surfaces may be significant over time. We select initial values for particle loading of 10 $\mu g/m^3$ and 10 $\mu g/m^2$ for the air and surfaces, respectively, following the approach of Bennett and Furtaw [36]. The deposition and resuspension rates are also taken from Bennett and Furtaw based on particle size bins of 0 to 1 μm and 1 to 2.5 μm for deposition and particle size bins up to 10 μm for resuspension.

Given a specified source strength and duration, and/or starting concentrations in each compartment combined with the parameters listed in Table 5, the mass balance equations (Eqs. 6 and 7) can be solved for the time-dependant concentrations in each compartment. Equations 6 and 7 can be rewritten in the form of a system of coupled first-order inhomogeneous differential equations [37] such that Eq 6 becomes

$$\frac{dy_1}{dt} = J_1 - k_{11}y_1 + k_{12}y_2 \qquad \text{Eq. 8}$$

and Eq 7 becomes

$$\frac{dy_2}{dt} = J_2 + k_{21}y_1 - k_{22}y_2 \qquad \text{Eq. 9}$$

where J_i are the volume normalized continuous source terms (mol m^{-3} d^{-1}), y_i are the concentrations (mol m^{-3}) and k_{ij} are rate constants for transfer and transformation (d^{-1}).

For a multi-phased exposure event (i.e., including step changes in the constant source term or repeated treatments such as the application of an insecticide to the surface), the start time ($t = t^*$) for each phase is defined as $t^* = t_{(1)}, t_{(2)}, \ldots t_{(n)}$, where $t_{(1)}, t_{(2)}, \ldots t_{(n)}$, are the times when the source undergoes a step increase or decrease or a broadcast application is made to the surface and n is the total number of source changes or phases in the modeling simulation. The initial concentrations in each compartment at the beginning of each phase are designated y_i^* and each rectangular (i.e., constant) source term, defined as J_i^*, applies to the duration of the phase beginning at time $t = t^*$. Given t, t^*, y_i^* and J_i^* for each phase of the event, a general analytical solution for the time dependent concentrations in air, $y_1(t)$, is

$$y_1(t) = \frac{\exp[-g_2(t-t^*)] - \exp[-g_1(t-t^*)]}{gg_{12}} \times \left(k_{12}y_2^* - k_{11}y_1^*\right)$$

$$+ \frac{g_1\exp[-g_2(t-t^*)] - g_2\exp[-g_1(t-t^*)]}{gg_{12}} \times y_1^*$$

$$+ \left\{ \frac{\dfrac{1-\exp[-g_2(t-t^*)]}{g_2} - \dfrac{1-\exp[-g_1(t-t^*)]}{g_1}}{gg_{12}} \right\} \times \left(k_{12}J_2^* - k_{11}J_1^*\right)$$

$$+ \left\{ \frac{\dfrac{1-\exp[-g_2(t-t^*)]}{g_2/g_1} - \dfrac{1-\exp[-g_1(t-t^*)]}{g_1/g_2}}{gg_{12}} \right\} \times J_1^* \qquad \text{Eq. 10}$$

and the time dependent concentration in the surface compartment, $y_2(t)$, is

$$y_2(t) = \frac{\exp[-g_2(t-t^*)] - \exp[g_1(t-t^*)]}{gg_{12}} \times \left(k_{21}y_1^* - k_{22}y_2^*\right)$$

$$+ \frac{g_1\exp[-g_2(t-t^*)] - g_2\exp[-g_1(t-t^*)]}{gg_{12}} \times y_2^*$$

$$+\left\{\frac{\frac{1-\exp[-g_2(t-t^*)}{g_2}-\frac{1-\exp[-g_1(t-t^*)}{g_1}}{gg_{12}}\right\}\times\left(k_{21}J_1^*-k_{22}J_2^*\right)$$

$$+\left\{\frac{\frac{1-\exp[-g_2(t-t^*)}{g_2/g_1}-\frac{1-\exp[-g_1(t-t^*)}{g_1/g_2}}{gg_{12}}\right\}\times J_2^* \qquad \text{Eq. 11}$$

where the rate constants, k_{ij} (d^{-1}) and *Eigenvalues*, g_i (d^{-1}) in equations 10-11 are defined in Table 6.

Table 6 Variables used in dynamic solution of the two-compartment mass balance

Overall rate constants (d^{-1})

$$k_{11}=\left(R_a+\frac{f}{V_a}+\frac{U_{sa}A_{sa}}{V_a}+v_{da}K_{da}\rho_{da}\right) \qquad k_{12}=\left(\frac{U_{sa}A_{sa}}{K_{sa}V_a}+\frac{v_{dc}K_{dc}\rho_{dc}A_{sa}}{V_a}\right)$$

$$k_{21}=\left(\frac{U_{sa}A_{sa}}{V_s}+\frac{v_{da}K_{da}\rho_{da}V_a}{V_s}\right) \qquad k_{22}=\left(R_s+\frac{U_{sa}A_{sa}}{K_{sa}V_s}+\frac{v_{ds}K_{ds}\rho_{ds}A_{sa}}{V_s}\right)$$

Eigenvalues in eqs 10 and 11

$$g_1=0.5\times\left(k_{11}+k_{22}+gg_{12}\right) \qquad g_2=0.5\times\left(k_{11}+k_{22}-gg_{12}\right)$$

$$gg_{12}=\sqrt{\left(k_{11}-k_{22}\right)^2+4k_{12}k_{21}}$$

This system of equations is written into a spreadsheet providing a simple tool to explore the fate of insecticides applied to surfaces in the airliner cabin environment.

4.3. Modeling assessment of insecticide fate in aircraft

The dynamic 2-box model described above can be used to explore several factors related to the behavior of a semi-volatile organic chemical (SVOC) in the defined system. The following subsections present a series of case studies illustrating and exploring 1) the overall fate or persistence of different insecticides applied in the aircraft cabin, 2) the time history concentration of a single aerosol application of phenothrin and permethrin, 3) the time-history concentrations following multiple aerosol applications that may accumulate in surfaces 4) the time-history

concentration of a single residual application of permethrin and 5) the time-history concentrations of repeated residual treatments.

4.3.1. Overall persistence of insecticides in the aircraft cabin

The overall rate constants or eigenvalues, g_1 and g_2 in Table 5, combine all fate and transport processes that are included in the mass balance into two rate constants for the system. The smaller of these rate constants ultimately controls how fast the system will respond after a change in source or initial application. In general, the rate constant g_1 represents the air compartment and g_2 is an indication of the chemical's fate in the surface compartment. The time to steady-state (t_{ss}, days) in the system after a change is made to the source or initial conditions is an indication of the overall persistence of the chemical in the airliner cabin and can be approximated as

$$t_{ss} \sim 3/\min\{g_1, g_2\} \qquad \text{Eq. 12}$$

This value is independent of the application method (aerosol spray in air or a broadcast application to a surface, whether continuous or intermittent) or the amount of insecticide applied. The t_{ss} also provides an indication of how rapidly the cabin would clear of insecticide if treatments were halted.

Using the chemical and environmental property values described in Tables 1 and 5, we tested the list of insecticides to determine t_{ss} for each chemical in the model aircraft cabin. The results are summarized in Table 7 for three cases including a typical ventilated cabin, a period with ventilation off and a ventilated cabin with chemical degradation in the surface compartment.

Table 7 Overall persistence (days) of chemicals in aircraft cabin

Name	*Ventilation on (ACH = 13.5 d^{-1})*	*Ventilation off (ACH = 0.5 d^{-1})*	*Ventilation on with reaction (R_2 = 0.07 d^{-1})*
prallethrin	1.6	9.1	1.5
allethrin	10.9	61.8	8.7
tetramethrin	3.6	20.6	3.3
resmethrin	0.6	3.4	0.6
phenothrin	41.2	242.7	21.0
permethrin	133.3	807.9	32.4
cypermethrin - beta	36.2	203.4	19.6
esfenvalerate	692.8	4032.4	40.4
bifenthrin	47.6	531.0	22.6
cyfluthrin	3082.0	22048.9	42.3
cyhalothrin	782.0	6440.7	40.6
deltamethrin	164.6	925.6	34.0

The physiochemical properties of the insecticides are listed in Table 1. The first results column in Table 7 gives the persistence assuming a long-term average air change rate as described in Table 5 while the second column uses an ACH representative of an idle aircraft. Both cases have no degradation. The last column shows results for the ventilated aircraft with a moderate degradation rate constant applied in the surface compartment (half-life ~ 10 days) for all chemical. The results are illustrated for comparison in Fig. 4. The results illustrate that 1) many of

the insecticides can be highly persistent in the aircraft cabin environment, 2) aircraft ventilation represents an important removal mechanism in the system even though much of the chemical is sorbed to/in the surface compartments and 3) for those compounds that are strongly sorbed to/in the surfaces, even a moderate reaction rate can significantly reduce the overall persistence of the chemical.

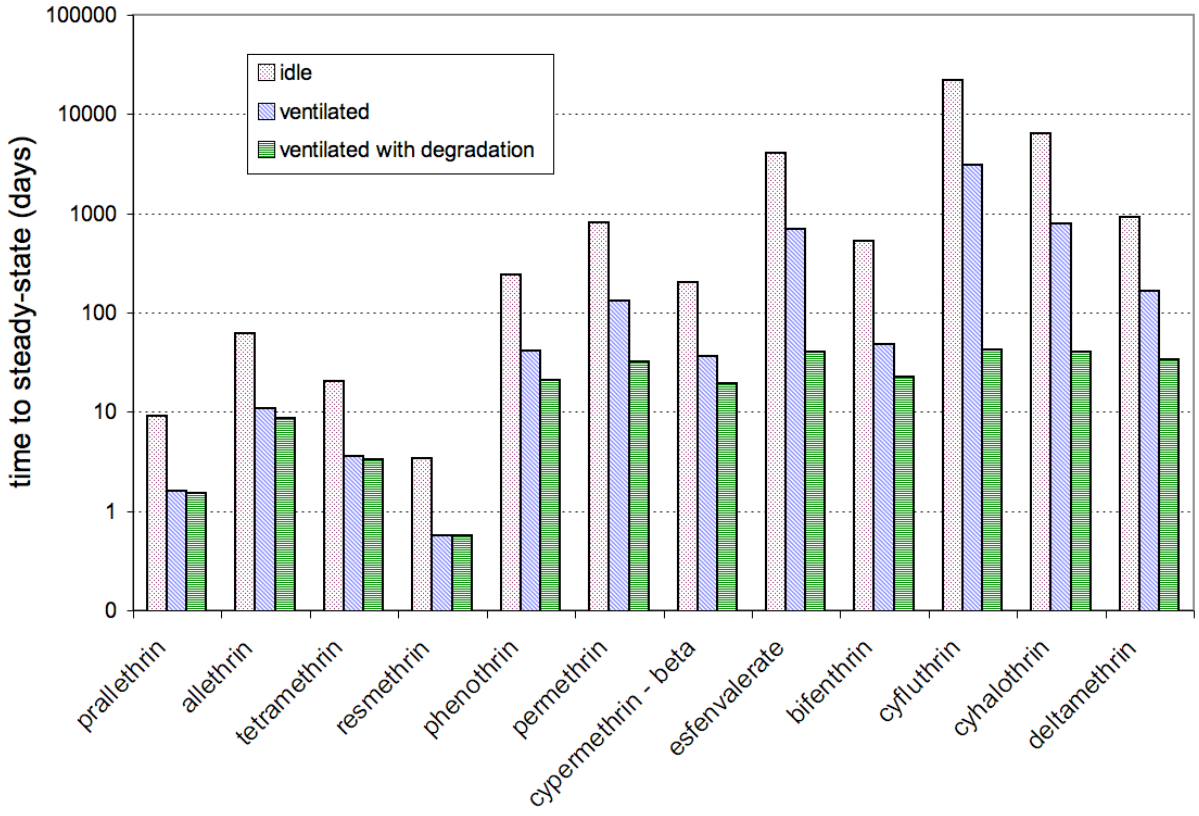

Figure 4 Comparison of overall persistence for insecticides released into the cabin environment with different ventilation and chemical reaction conditions.

4.3.2. Time-history concentrations for single aerosol application

The dynamic two-box model can be setup to represent a single application to the air for a fixed duration similar to what would occur for the aerosol insecticide application methods. We assume that the insecticide is sprayed uniformly in the cabin for 15 minutes and a total of 10 mg active ingredient is applied per m^3 of cabin volume and model the resulting concentrations in the air and surface compartments are tracked for 60 minutes. The physics of the spray droplets is ignored and the active ingredient is assumed to be instantly well mixed in the cabin air and subject to the transport processes described in the mass balance. The process is repeated for both phenothrin and permethrin using the environmental conditions described in Table 5 except that the starting surface concentration (C0_2) is zero.

The resulting time-history concentration profile over a 60 minute period for phenothrin and permethrin are shown in Figure 5. The concentrations of both chemicals increase rapidly in the air during active spraying reaching a maximum concentration above 2000 $\mu g/m^3$ but then the

concentrations of both chemicals also drop rapidly after spraying stops reaching values less than 0.5 $\mu g/m^3$ within 40 minutes. The surface loading for a single application to the cabin air reaches a maximum value approximately 30 minutes after spraying is initiated (15 minutes after spraying ends) and the surface loading of phenothrin is slightly lower than that of permethrin. The maximum surface loading after a single application is less than 0.15 $\mu g/cm^2$ for each chemical and this accounts for only about 0.5% of the total applied mass (285 mg) in the cabin. It is likely that the remaining material is removed by ventilation before it has a chance to deposit. Some fraction of this material will likely deposit in the ventilation path and on the filters and it is not known how long this residue might persist or if it will be recirculated back into the cabin. In this exercise we assume that once the chemical is removed from the cabin it does not return.

Although the insecticides are rapidly cleared from the cabin air following application, the residue that deposits to surfaces inside the cabin is much more persistent. To compare the persistence of the two chemicals following a single application, the time axis is extended to 48 hours in Figure 6. The results indicate two things. First, even in the absence of chemical degradation pathways, the phenothrin is cleared from the system somewhat faster than permethrin. Second, after the initial and rapid clearance of the chemicals from the air compartment following an application, the longer-term concentration in the air is dependant on, or controlled by, the average surface loading in the cabin. Even two days after application, the air concentrations in the cabin for permethrin and phenothrin are above 300 ng/m^3 and 100 ng/m^3, respectively and the surface loadings are only reduced roughly 20% from the maximum value.

In summary, although the initial loading in the cabin environment after a single application to the air is only a fraction of what is applied, the material that is loaded on surfaces can potentially remain for an extended period and the concentrations in the air appear to be related to the average surface loading. Given that only the fabric surfaces are included in the assessment, the actual loading are likely to be lower. But the overall behavior of the system is not expected to differ much.

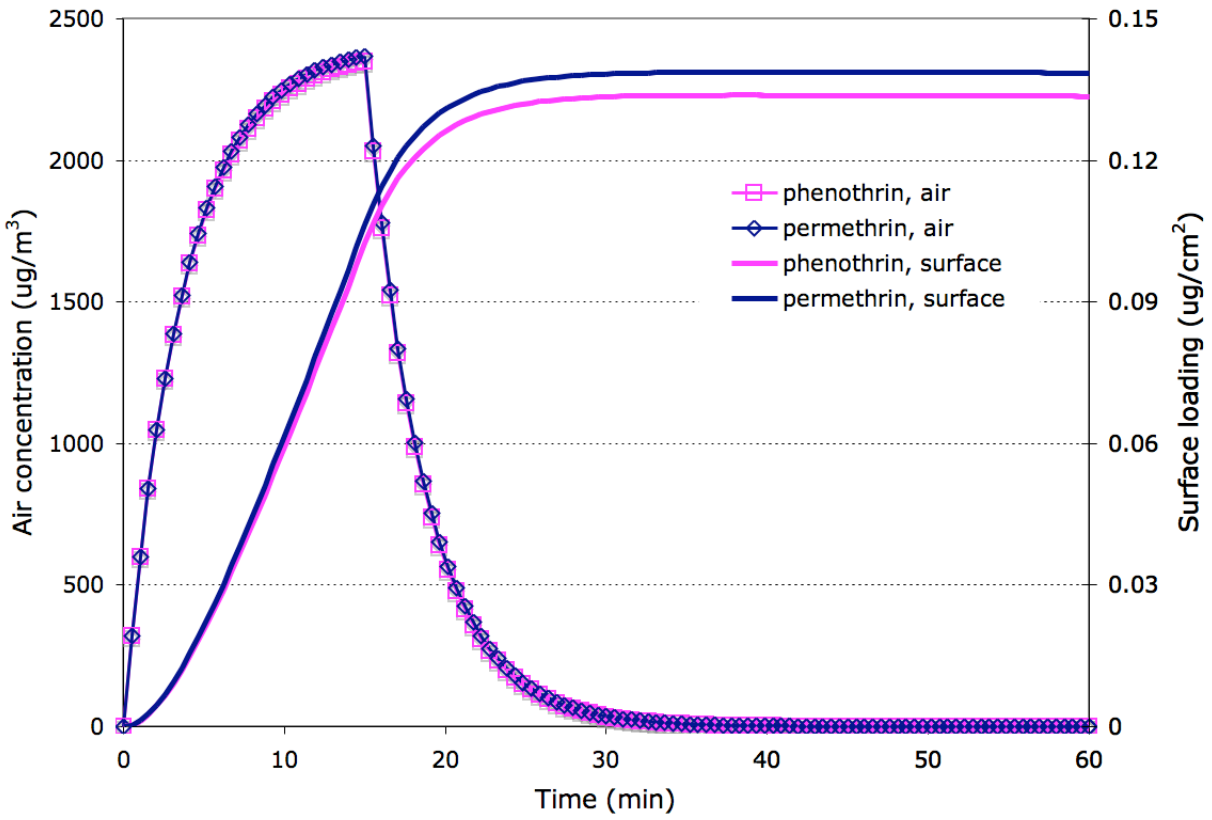

Figure 5 Time-history concentration for single (15 minute) well mixed aerosol application of phenothrin or permethrin over a 60 minute window.

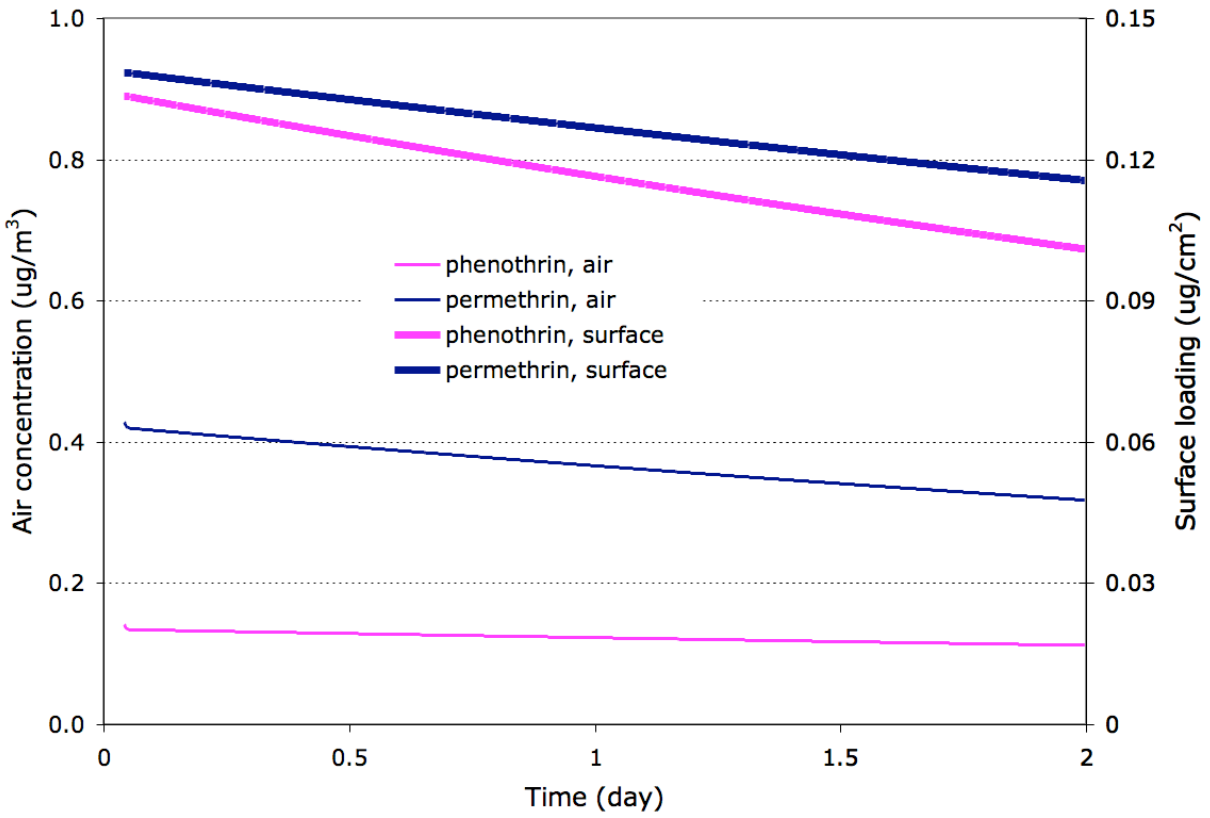

Figure 6 Extended time-history concentration starting one hour after a single aerosol application (shown in Fig. 5) to cabin air compartment.

4.3.3. Time-history concentrations for repeated aerosol application

Given the slow removal of residue from the cabin environment, even if a small fraction of the mass applied during each application deposits on surfaces, there is a potential for continued surface loading over repeated treatment. To explore this, we use the same application procedure and conditions as described above with ventilation on and with a reaction-rate constant in surfaces of 0.07 d^{-1}. But in this case the application is repeated at 48 hour intervals using phenothrin. The actual frequency of aerosol treatment in a given aircraft is not known (information is not publicly available) but we assume that the same aircraft will not travel to a destination requiring aerosol application (top-of-decent, blocks-away, or on-arrival) more than once every 48 hours. Figure 7 illustrates the time-history concentration in the air and surface compartments resulting from four consecutive treatments occurring every other day.

Because of the rapid air exchange in the cabin, the air concentration spikes during application do not increase significantly with time (repeated treatments) but the surface loading does increase with each application. To explore the long-term trend in the surface loading from repeated aerosol treatments at consistent intervals we plot the maximum surface loading following each treatment along with the minimum loading just prior to the next treatment in Figure 8. The model line fit through both uptake curves takes the form $C_t=C_{ss}(1-\exp^{-kt})$ where C_t is the concentration or loading at time = t, C_{ss} is the steady-state loading and k is the rate constant for uptake.

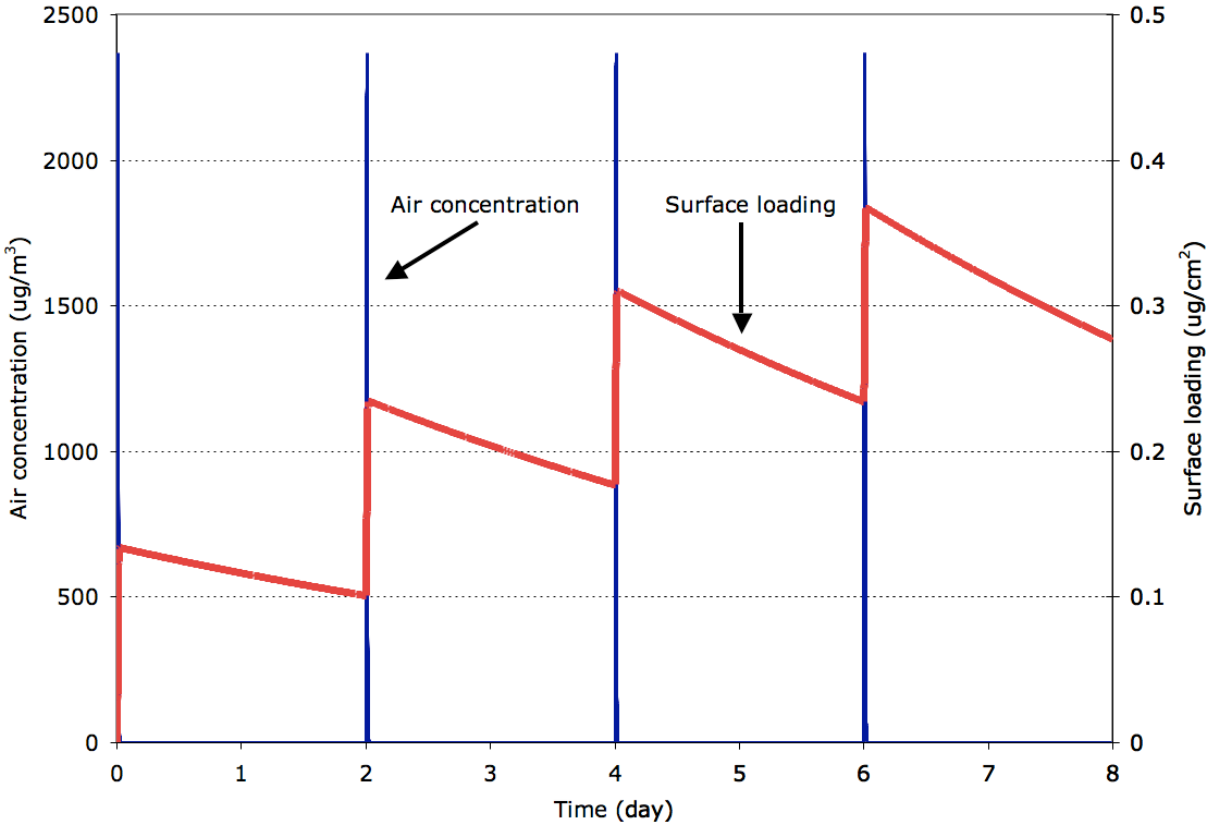

Figure 7 Time-history concentrations for phenothrin in air and the surface loading following repeated insecticide treatments in the cabin air. The spikes in the air occur during each application and the incremental increase in the surface loading is a result of deposited material from the air.

The model line that is fit through the two uptake curves for repeated applications of phenothrin has a rate constant of 0.14 day^{-1}. Using the definition of time to steady state presented earlier (Eq. 12) and the rate constant from the fitted uptake models in Fig 8, the resulting t_{ss} for phenothrin loading of the surface following repeated applications is 21 days. This is the same value that was obtained for the system persistence in Section 6.3.1 demonstrating that the time to steady state depends only on the overall rate constant in the system even for intermittent applications as long as those applications are of a constant frequency and magnitude. If the application frequency increases, the time to steady state would not change but the steady state loading in the system would increase. Similarly, if the frequency was decreased, the steady-state loading would be expected to decrease. But again the time to reach steady state loading would not change.

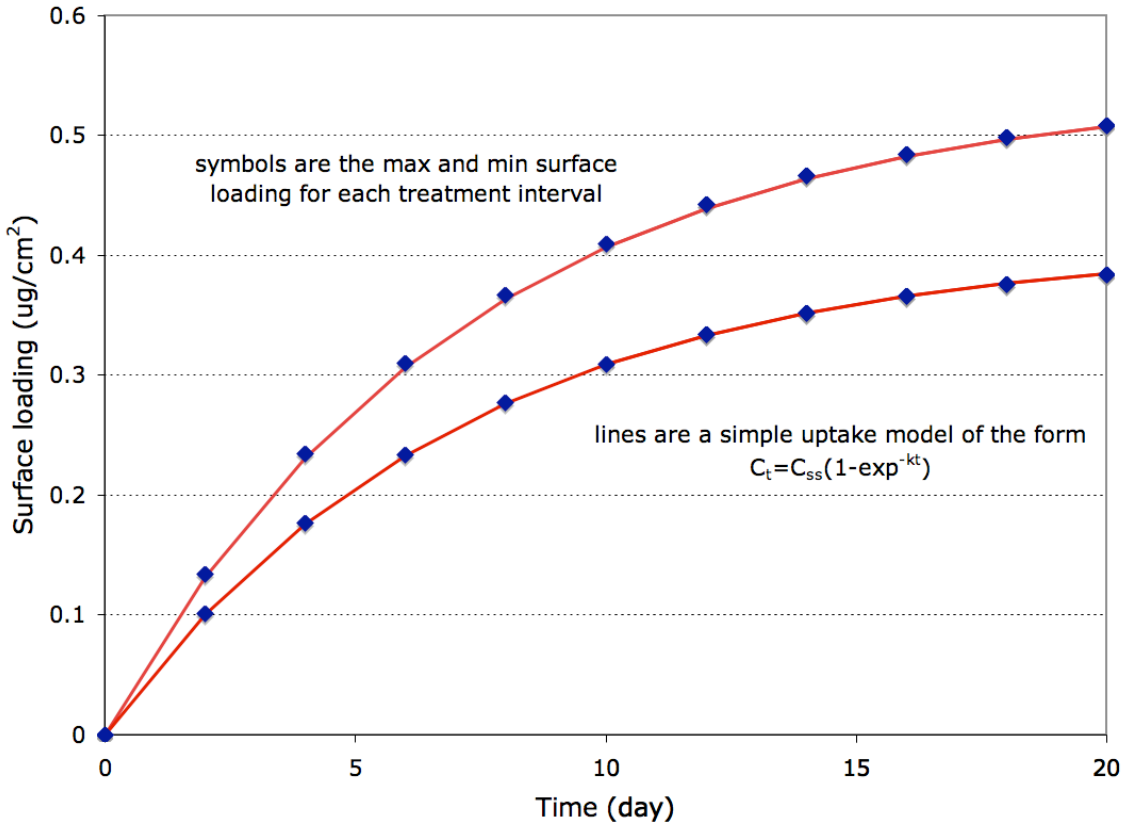

Figure 8 The maximum and minimum surface loading of phenothrin for each treatment interval (solid symbols) and a simple uptake model (line) fit to the data by adjusting the uptake rate constant and steady-state concentration. The rate constant (k) for both the max and min surface loading is equal to 0.14 day^{-1} which converts to an overall persistence of 21.4 days, which is similar to the overall clearance rate for the system.

4.3.4. Time-history concentrations for single residual application

The other application method that can be used indoors is to treat surfaces directly, i.e., residual, broadcast, of fogging in sealed aircraft. These applications can be either episodic or at regularly scheduled intervals. The same questions regarding the time-history concentrations exist for this direct treatment method as for the aerosol treatments that were evaluated above. In this case we assume that the active ingredient is applied directly to the surface. Although the aircraft has a number of different surfaces, we focus here on the fabric surfaces (carpet and seats). The other surfaces in the aircraft cabin will likely be treated at the same time but the impervious nature of these "hard" surfaces will ultimately result in a much smaller compartment volume (thickness of organic film or effective thickness of dust on Tedlar surfaces for example). This will result in a lower capacity of the surface for holding the chemicals and, as a result, a shorter t_{ss}. The overall effect of ignoring these impervious surfaces in this initial modeling is that the response time of the system may actually be somewhat shorter and the air concentrations may be slightly higher. But the overall pattern of the time-history concentrations are not expected to change significantly.

Given the direct residual application to the surfaces, the mass balance model "sees" the average loading or starting concentration in the surface compartment. Therefore, any spatial variation in the initial loading should not affect the outcome. However, we do have to assume that the applied chemical is uniformly mixed into the full depth of the surface compartment instantly and that all of the chemical is available for exchange with the overlying air compartment throughout the duration of the modeling run. This means that there is no irreversible sequestration of chemical in the surface compartment. To test the influence of this loss pathway we run the assessment twice following an initial direct application of permethrin. The assessment is run for 100 days following application both with surface reactions (half-life for loss in surface ~ 10 days) and without degradation in the surface compartment. In both cases we use the standard ACH representing an actively used aircraft as listed in Table 5. The results are shown in Figure 9.

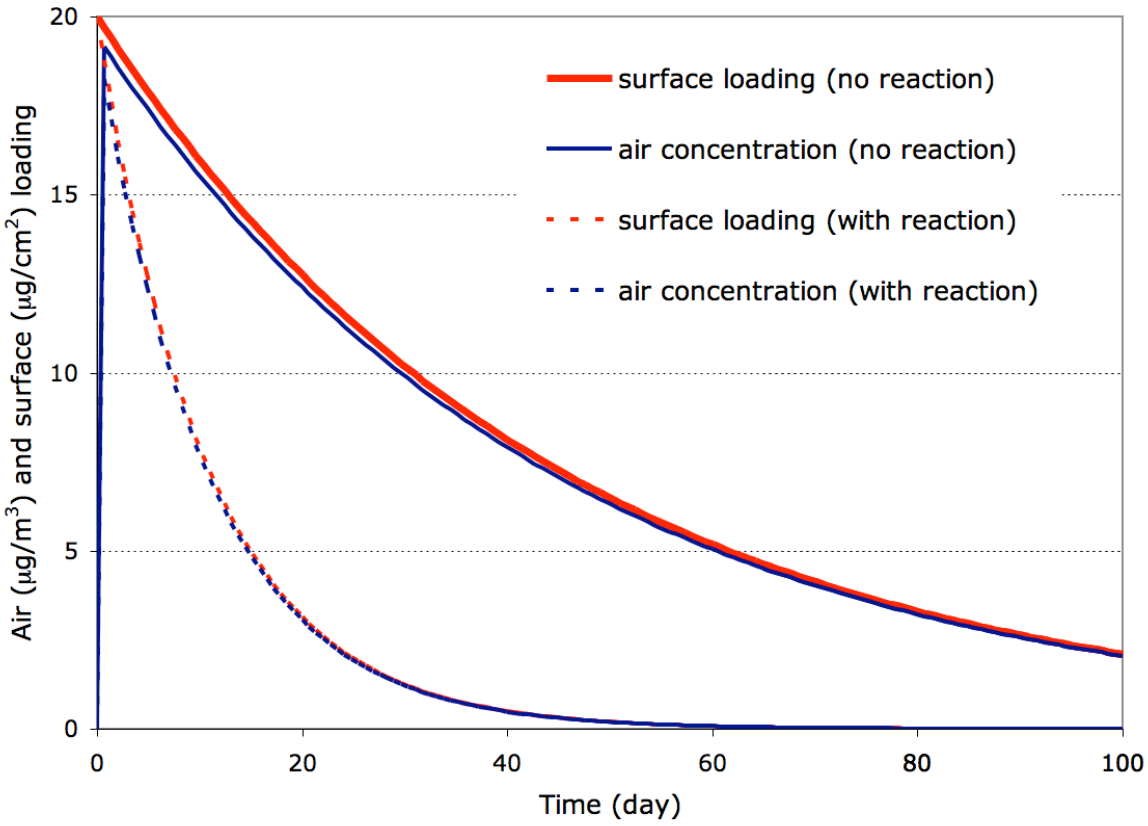

Figure 9 Time-history concentration of permethrin following a single residual treatment (20 mg/cm^2) for the case with no degradation or sequestration in the surface (solid lines) and with a moderate reaction rate (dash line).

Several observations can be made from the results in Figure 9. First, the persistence of permethrin in the aircraft cabin will likely lead to accumulation from repeated treatments if the frequency of treatment is more often than the time to steady state in the system (i.e., 32 days and 133 days with and without degradation in the surface, respectively). Second, reaction and/or sequestration in the surface can significantly alter the concentration profile. Along with this, we found that chemical degradation in the air compartment has no influence on the concentrations or persistence of the

SVOCs in the system. This is likely due to the rapid removal rate by ventilation for chemicals that are in the air (gas- or particle-phase). Third, the concentration in the air for residual applications closely tracks the surface loading in the aircraft suggesting that an air measurement can provide an indication of the surface loading in the aircraft.

4.3.5. Time-history concentrations for repeated residual application

The residual application scenario described above was repeated several times at 56 day intervals to assess the accumulation of insecticide in the aircraft. The model was run assuming no degradation. The air concentration and the surface loadings were tracked for approximately 280 days. Similar to the other repeated insecticide applications, the results in Fig. 10 show that as the insecticide loading and concentrations accumulate but the time that it takes to reach steady-state (max and min) concentrations are again controlled by the response time of the system (133 days for permethrin without degradation) and not the application method or application amount. In this case the final maximum surface loading attained after repeated applications on an eight week interval is about 40% greater than the initial 20 μg/cm^2 application. Additionally, the minimum loading at steady-state after repeated residual applications is approximately 8 μg/cm^2.

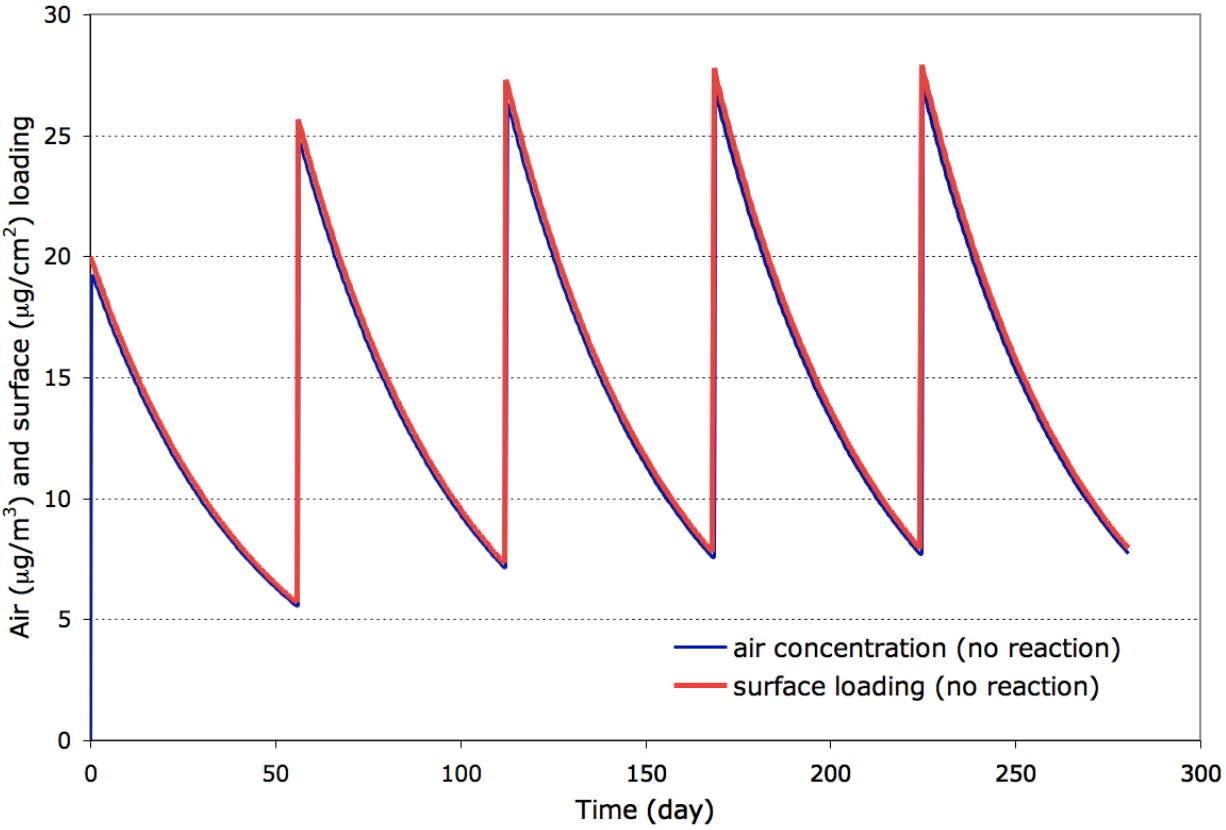

Figure 10 Concentration profile following repeated residual application of permethrin.

4.4. Summary findings of modeling exercise

The modeling in this section illustrates the behavior of insecticides in a dynamic 2-box model representing the aircraft cabin environment. Clearly the level of detail of the modeling can be increased by adding more compartments and transport processes but the existing data on application rates and methods and on details related to the cabin environment are not sufficient to support a more detailed model for SVOCs at this time. However, the model does demonstrate the exposure implications for insecticides that accumulate in surfaces following repeated applications. The magnitude of this accumulation depends on the method (residual or aerosol), amount and frequency of insecticide application. The magnitude of accumulation also depends on the response time in the air/surface system or time to steady state and this response time depends on a number of physiochemical and environmental properties, many of which are either unknown, uncertain or expected to be highly variable across the fleet. However, if the response time in the cabin is known then it will be the same for any treatment method, frequency and application rate.

Another finding in the modeling exercise was that although the air-compartment concentrations are generally low, they provide a consistent integrated measure of the average loading in the aircraft. This indicates that with adequate detection limits and a wide enough sampling coverage in the aircraft, measurements of the air concentration could be an effective and efficient approach for surveying an aircraft for the presence of insecticides. Given adequate calibration, the air concentration measurements not only provide an indication of the presence of insecticide residues, but can also provide a first approximation of the SVOC exposure concentrations experienced by occupants of the space.

Finally, although the modeling system described here can be used to estimate average exposures during applications and long-term exposures from insecticide residues on aircraft, we note that the improper application of insecticides in the aircraft cabin and inconsistencies in ventilation procedures following an application can still result in significantly elevated exposures. These incidents have led to odors and visible insecticide residues on surfaces [21] that are related to complaints reported by flight attendants and crew. However, quantifying the magnitude and frequency of these episodic exposures cannot be determined with a model alone. Understanding these episodic events would likely require some level of surveillance in combination with modeling.

5.0 Conclusions

The literature review presented in this report found that although there is agreement regarding the need to control the unintended transport of insects on aircraft, there are clearly opposing views as to the efficacy and risks associated with chemical disinsection practices. Understanding risks associated with any chemical application requires knowledge of both toxicity and exposure. Pyrethroids are the most commonly used class of insecticides on aircraft. Our understanding of the toxicity of pyrethroids continues to evolve but knowledge about exposure on aircraft is almost completely lacking. A large number of pyrethroid applications have been studied to characterize potential exposure in other residential, commercial and occupational environments but only a few studies have considered applications on aircraft and these are focused on a single application

method (aerosol disinsection). Information on residual treatment or treatments used in the domestic fleet are completely lacking.

Given the ongoing use of chemical disinsection, or the option to use disinsection, and the continued debate over the potential health risks associated with insecticide use on aircraft, it is surprising that scientifically defensible exposure data are still lacking. Insecticide use in the airline industry offers a unique case where a systematic monitoring effort could help elucidate the relationship between indoor insecticide treatments and exposure. There are a number of characteristics of the aircraft exposure scenario that make it well suited for a study linking insecticide use to exposure. These characteristics include 1) the aircraft cabin and flight deck where exposure occurs is highly controlled and well mixed, 2) although there is variability in the insecticide application practices, documentation of the amount and frequency of insecticide use should be available, at least for routes requiring disinsection, 3) the potentially exposed population (flight attendants, crew and passengers) can be separated into control and treatment groups by knowing which aircraft are treated, and 4) the activity patterns of the exposed individuals on a given aircraft and route are relatively homogeneous across the cohort for passengers or crew.

When developing a sampling strategy to understand chemical exposures on aircraft, there is a trade-off between collecting samples with a high degree of spatial and temporal resolution that are narrowly focused (i.e., only a few aircraft) and collecting samples with lower resolution but with a wider coverage. Active sampling methods are available and have been used on aircraft for measuring concentrations with relatively high spatial and temporal resolution but these methods require a technician to accompany each sampler on each flight making it difficult to collect the number of samples needed for observational studies where information about insecticide applications is lacking. With the goal of expanding the coverage of aircraft in future monitoring studies, this report describes the initial development of a simple and practical tool for monitoring SVOC loading using passive sampling technology. In addition, a dynamic two-compartment mass balance model was developed and demonstrated for SVOCs in the aircraft cabin environment. The model indicates that insecticides can accumulate on surfaces following repeated applications. The modeling also shows that the average loading of insecticides in the aircraft cabin can be determined from measurements of the air concentrations.

The findings in this report lead to several suggestions for characterizing the relationship between insecticide use on passenger aircraft and exposure levels present in the cabin environment. These are provided in the following sections.

5.1. Screening level evaluation of insecticide loading on aircraft

Given the available technology for active air sampling of SVOCs on aircraft, a screening level in-flight monitoring campaign on a limited number of flights would be informative. This sampling should be conducted in conjunction with surface wipe sampling to determine surface residues where feasible and begin to characterize the relationship between air concentrations and surface loadings. Ideally the tested aircraft will have insecticide treatment records available through airline industry participation, but in the absence of records that identify target chemicals it is important to screen for a wide range of insecticides including current use insecticides (see Table 1) and legacy chemicals (e.g., organophosphates and organochlorines) that may persist in the cabin.

This recommendation points to the critical need for airline industry participation in any study aimed at characterizing in-flight exposure concentrations on aircraft. Collection of initial measurements on a limited number of flights was one of the goals of the current study but we were not able to gain access to treated aircraft.

In the absence of industry participation, there would need to be an effort to identify a surrogate environment (i.e., a test chamber, an aircraft mockup or an active military aircraft) that can be studied with repeated insecticide applications to characterize the link between insecticide use and exposure concentrations.

5.2. Fleet level evaluation of insecticide loading on aircraft

Although a limited number of measurements for aerosol applications are available, monitoring of aircraft that are treated intermittently in the domestic fleet or regularly on routes requiring disinsection are completely lacking. If the results from a screening level monitoring assessment indicate that aircraft are in fact being treated in the domestic fleet, and insecticides are accumulating on surfaces, then a more extensive study is warranted. It would be necessary to use a simpler tool for collecting measurements to maximize the coverage of the fleet. Widespread deployment of passive samplers in the domestic fleet can provide a baseline for the distribution of exposure concentrations particularly if complementary surface samples are also collected on select aircraft.

The thin-film polymer coated glass samplers described in this report still require calibration and testing before being field ready. The final development of the samplers would require airline industry participation for identifying locations to deploy the samplers in actual aircraft and the environmental conditions experienced at the selected locations in order to finalize the housing design for the samplers and the calibration conditions. If development and calibration of the samplers is successful, it is anticipated that average surface loading and occupant exposure in the aircraft would correlate with long-term integrated air samples [28]. A dataset of integrated air samples collected using passive samplers in a statistically representative set of passenger aircraft would provide a first approximation of the extent of exposure to insecticides.

5.3. Alternative approach to in-flight measurements on aircraft

If in-flight measurements are not feasible for either active sampling or passive sampling and a reliable surrogate environment (chamber or aircraft mockup) is not identified, then an alternate approach to determining exposure concentrations would be to collect samples on aircraft that are idle. The modeling described in this report demonstrates that it is possible to estimate average surface loadings in an aircraft from air concentrations.

Annual utilization reports indicate that aircraft spend a least eight hours per 24 hour period parked overnight at airports. Given access to aircraft through airline industry participation, this idle period provides an opportunity for a controlled sampling event that does not impact flight operations, crew or passengers. Although the conditions in the cabin during the idle period are much different than during in-flight periods, the measurements can be used with modeling to estimate exposure concentrations during active periods. Ideally, the initial sampling events in the idle aircraft would include multiple active samplers in different areas of the aircraft to measure air concentrations (gas and particle phase), a tracer measurement to determine the air exchange rate during sampling, and several different surface wipe samples collected from different areas of the

cabin. The combination of air samples, air exchange rate measurements and surface wipe samples would provide a measure of the average surface loading in the aircraft, the variability of surface residue levels throughout the aircraft and the relationship between measured air concentrations and surface loadings. Once the relationship between surface loadings and air concentrations are determined, future sampling events can be reduce to just include air sampling and air exchange rate measurements and models would be used to estimate the distribution of insecticide loadings in the aircraft and the air concentrations during flight. Repeated measurements collected over time from the same aircraft can provide information about the residence time of insecticides in the cabin environment.

Monitoring during idle periods would potentially increase the number of aircraft that could be tested, increase the level of sampling resolution on each aircraft, and minimize the impact on flight operations.

5.4. Field measurements of biological markers of exposure

If airline industry participation is not available then it may be possible to assess exposure directly through biomarker measurements collected from flight attendants, crew and/or passengers. A number of studies have demonstrated the use of biomarkers to characterize exposures to pyrethroids indoors [24, 35-37, 39, 41]. Pyrethroid insecticides are quickly metabolized in humans to produce a variety of conjugates and free acid forms of the insecticide that are excreted in urine and these metabolites provide a direct marker of exposure. Applying a urinary biomarker approach to airline crewmembers and passengers would have challenges such as the storage and transport of samples while on a layover but the results would provide a useful tool for exploring difference between the background population and individuals who spend extended periods of time on aircraft.

The profiles of conjugated forms of the insecticide metabolites and the amount of the free acid vary among individuals. Table 1 shows the free acid metabolites formed in urine from exposure to permethrin, *cis*-permethrin, *trans*-permethrin, and d-phenothrin.

Table 8 Biomarker urinary metabolites for pyrethroid insecticides

Pyrethroid	Urine metabolite (acronym)
Permethrin	3-phenoxybenzoic acid (3-PBA)
cis-Permethrin	*Cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (*cis*-DCCA)
trans-Permethrin	*Trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (*trans*-DCCA)
d-phenothrin	Chrysanthemumdicarboxylic acid (CDCA) 4-Fluoro-3- phenoxybenzoic acid (F-PBA)

Because pyrethroids are quickly metabolized and excreted, flight attendants and crew provide a unique opportunity to measure uptake of insecticides from treated aircraft. By collecting samples prior to and immediately following flights (or during long flights) a relevant marker of onboard

exposure can be established. In addition to providing a clear marker of exposure, the biomarkers are important as a means to verify predictions based on exposure concentrations and intake rates and to provide a more relevant indication of dose for exposed individuals.

A biomarker study would have several uses including 1) a source of new data for verification of exposure predictions based on environmental markers, 2) an opportunity to compare an exposed cohort with the background US population and/or a select cohort of flight attendants that work on "untreated" planes and 3) a tool or method for retrospective quantification of exposure to insecticide incidents (e.g., odors or evidence of puddles in crew bunks). This information would also be helpful in understanding pyrethroid exposures in other environments such as residences, schools, and child care facilities.

Three methods exist for measuring pyrethroid metabolites in urine. These include GC/MS [37, 41, 65, 66], LC/MS [45] and Immunoassays [46]. The GC/MS method provides the greatest sensitivity (as low as 0.05 μg/L for some metabolites) and the best resolution of the various metabolic forms of the analyte. A recently developed assay can resolve all known metabolites in one GC/MS run [47], but requires access to a high resolution GC/MS using negative chemical ionization mode. For both LC and GC mass spectrometry assays, the urine sample is prepared in three steps: 1) acid or enzymatic hydrolysis of all conjugated forms of the metabolites, 2) organic (or solid phase) extraction, and 3) derivatization of the metabolites to enhance detection. Leng [47, 48] reports that urine samples may be stored frozen at –20 C for up to a year before analysis and that derivatized samples may be stored at 4 C for one month before analysis.

There seem to be very few, if any, technical barriers to a biomarker study of flight attendants, crew and/or passengers on treated aircraft. Ideally the biomarker study would be conducted with airline industry participation on aircraft with known insecticide treatment history and/or having simultaneously measured exposure concentrations in the cabin but industry participation may not be required.

5.5. Alternate methods of vector control on aircraft

Even in the absence of exposure data on aircraft, there are advantages to reducing chemical use in indoor environments. Most agree that it is prudent to limit the transmission of insects (either invasive species or disease vectors) between different regions of the world by aircraft. The literature review presented in this report found that pest control is usually accomplished, when necessary, using chemical methods as recommended by the WHO. Despite the fact that chemical disinsection has been used in the airline industry for many years, there are both economic and public health reasons to reduce chemical exposure whenever possible.

Recently, several organizations including the USDA and USDOT have evaluated the use of mechanical disinsection methods as an alternative to the current chemical approach [49]. The International Convention on Civil Aviation (ICAO), which publishes International Standards and Recommended Practices, recently changed the wording of Standard 2.24 (Chapter 2 of Annex 9), (March 2004) to recognize the use of non-chemical methods of disinsection. In addition, at least some countries (Trinidad and Tobago for example) have shown an interest in using mechanical disinsection.

Advances have also been made recently in risk-based methods for identifying seasonality factors and routes where targeted vector control may be warranted [50]. Target vector control can lead to an overall reduction of insecticide use on aircraft.

As alternative approaches to insect control on aircraft emerge, it is important that all of the stakeholders who are involved in, responsible for, or potentially effected by insect control in the airline industry be inform about the background and status of these methods. There should be an ongoing and open dialogue through working groups, workshops and/or conferences about the successes and drawbacks of new technology or approaches. In addition to introducing the stakeholders to emerging technology, gathering information from stakeholders about concerns and operational issues could help advance opportunities for alternate approaches and accelerate the transfer of new technology for insect control on aircraft. The ultimate goal of such a dialogue would be to identify and apply safe and effective technologies for controlling the unintended transport of insects on aircraft.

6.0 References

1. Rayman, R.B., *Aircraft Disinsection.* Aviation, Space and Environmental Medicine, 2006. **77**(7): p. 733-736.

2. Gratz, N.G., R. Steffen, and W. Cocksedge, *Why aircraft disinsection?* Bulletin of the World Health Organization, 2000. **78**(8): p. 995-1004.

3. Riley, B., *Flyers Beware: Pesticide use on international and U.S. domestic aircraft and flights*. 2002, Northwest Coalition for Alternatives to Pesticides (NCAP): Eugene, OR.

4. USDOT, *Aircraft disinsection requirements (on-line)*. 2008, U.S. Department of Transportation (Last updated 12/5/2007): Washington, DC: http://ostpxweb.dot.gov/policy/SafetyEnergyEnv/disinsection.htm.

5. Kilpatrick, A.M., Y. Gluzberg, J. Burgett, and P. Daszak, *Quantitative risk assessment of the pathways by which west nile virus could reach Hawaii.* EcoHealth, 2004. **1**: p. 205-209.

6. HCA, *Mosquitoes in Hawai'i*. 2005, Hawaii Conservation Alliance: Position paper 2005-02.

7. WHO, *Report of the informal consultation on aircraft disinsection*. 1995, World Health Organization, International Programme on Chemical Safety IPCS: Geneva.

8. ICAO, *Aircraft disinsection and Aircraft disinsection practices survey*. 2001, International Civil Aviation Organization Facilitation Panel (FALP): Montreal.

9. MQS/AQIS, *Schedule of Aircraft Disinsection Procedures*. 2004: New Zealand, Australia.

10. Oldbury, D.J., *Deadly Cargo.* Environmental Health Journal, 2005: p. 22-24.

11. ADWG, *Aircraft residual disinsection protocol: a practical guid to the application of residual insecticides on aircraft*. 2001, Aircraft Disinsection Working Group: Manchester, UK.

12. Spicer, C.W., M.J. Murphy, M.W. Holdren, J.D. Myers, I.C. MacGregor, C. Holloman, R.R. James, K. Tucker, and R. Zaborski, *Relate air quality and other factors to comfort and health symptoms reported by passengers and crew on commercial transport aircraft (Part I)*, Battelle Science and Technology International. Columbus, OH. 2004, Amercian Society for Heating, Refrigerating, and Air Conditioning Engineers: Atlanta, GA.

13. Murawski, J., *Insecticide use in occupied areas of aircraft*, in *Air Quality in Airplane Cabins and Similar Enclosed Spaces*. 2005, Springer: Berlin / Heidelberg.

14. USEPA, *Reregistraton Eligibiligy Decision (RED) for Permethrin - Revised December 2007*. Prevention, Pesticides and Toxic Substances. U.S. Environmental Protection Agency: Washington D.C.

15. WHO, *Recommendations on the disinsecting of aircraft.* World Health Organization, Weekly Epidemiological Record, 1985. **60**(7): p. 45-47.

16. WHO, *Recommendations on the Disinsecting of Aircraft.* World Health Organization, Weekly Epidemiological Record, 1998. **70**(15): p. 106-111.

17. Berger-Preiβ, E., W. Koch, W. Behnke, S. Gerling, H. Kock, L. Elfein, and K.E. Appel, *In-flight spraying in aircrafts: determination of the exposure scenario.* International Journal of Hygiene and Environmental Health, 2004. **207**(5): p. 419-430.

18. Berger-Preiβ, E., W. Koch, S. Gerling, H. Kock, J. Klasen, G. Hoffmann, and K.E. Appel, *Aircraft disinsection: Exposure assessment and evaluation of a new pre-embarkation method.* International Journal of Hygiene and Environmental Health, 2006. **209**(1): p. 41-56.

19. NRC, *The airliner cabin environment and the health of passengers and crew*. 2002, National Research Council, Washington, DC: National Academy Press.

20. Sutton, P., X. Vergara, J. Beckman, and R. Das, *Occupational Illness among Flight Attendants Due to Aircraft Disinsection*. 2003, Occupational Health Branch; State of California Health and Human Services Agency Department of Health Services: Oakland CA.

21. Sutton, P.M., X. Vergara, J. Beckman, M. Nicas, and R. Das, *Pesticide Illness Among Flight Attendants Due to Aircraft Disinsection.* American Journal of industrial Medicine, 2007. **50**: p. 345-356.

22. Ecobichon, D.J., *Toxic Effects of Pesticides*, in *Casarett and Doull's Toxicology: Basic Science of Poisons*, M.O. Amdur, J. Coull, and C.D. Klaassen, Editors. 1991, Pergamon Press: New York.

23. Cecchine, G., B.A. Golomb, L.H. Hilborne, D.M. Spektor, and C.R. Anthony, *A review of the scientific literature as it pertains to Gulf War illnesses - Volume 8: Pesticides*. 2000, New York: RAND Corporation. 216.

24. Kilburn, K.H., *Effects of Onboard Insecticide Use on Airline Flight Attendants.* Archives of Environmental Health: An International Journal, 2003. **58**(6): p. 284-291.

25. Shafer, T.J., D.A. Meyer, and K.M. Crofton, *Developmental neurotoxicity of pyrethroid insecticides: Critical review and future research needs.* Environmental Health Perspectives, 2005. **113**(2): p. 123-136.

26. USEPA, *Permethrin & Resmethrin (Pyrethroids) TEACH Chemical Summary*. 2007, U.S. Environmental Protection Agency: http://www.epa.gov/teach/.

27. Horstmann, M. and M.S. McLachlan, *Initial development of a solid-phase fugacity meter for semivolatile organic compounds.* Environmental Science & Technology, 1992. **26**(1643-1649).

28. McKone, T.E., R. Castorina, M.E. Harnly, Y. Kuwabara, B. Eskenazi, and A. Bradman, *Merging models and biomonitoring data to characterize sources and pathways of human exposure to organophosphorus pesticides in the Salinas valley of California.* Environmental Science & Technology, 2007. **41**(9): p. 3233-3240.

29. Wilson, N.K., J.C. Chuang, R. Iachan, C. Lyu, S.M. Gordon, M.K. Morgan, H. Ozkaynak, and L.S. Sheldon, *Design and sampling methodology for a large study of preschool children's aggregate exposures to persistent organic pollutants in their everyday environments.* Journal of Exposure Analysis and Environmental Epidemiology, 2004. **14**: p. 260-274.

30. Namiesnik, J., B. Zabiegala, A. Kot-Wasik, M. Partyka, and A. Wasik, *Passive sampling and/or extraction techniques in environmental analysis: a review.* Analytical and Bioanalytical Chemistry, 2005. **381**(2): p. 279-301.

31. Shoeib, M. and T. Harner, *Characterization and comparison of three passive air samplers for persistent organic pollutants.* Environmental Science & Technology, 2002. **36**: p. 4142-4151.

32. Hunt, E.H. and D.R. Space. *The airplane cabin environment: Issues pertaining to flight attendant comfort*. in *International In-Flight Service Management Organization Conference*. 1994. Montreal, Canada: Boeing Company.

33. Hunt, E.H., D.D.H. Reid, D.R. Space, and D.F.E. Tilton. *Commercial airliner environmental control system: Engineering aspects of cabin air quality*. in *Aerospace Medical Association annual meeting*. 1995. Anaheim, California: Boeing Company.

34. Farrar, N.J., T. Harner, M. Shoeib, A. Sweetman, and K.C. Jones, *Field deployment of thin film passive air samplers for persistent organic pollutants: A study in the urban atmospheric boundary layer.* Environmental Science & Technology, 2005. **39**: p. 42-48.

35. Harner, T., N.J. Farrar, M. Shoeib, K.C. Jones, and F.A. Gobas, *Characterization of polymer-coated glass as a passive air sampler for persistent organic pollutants.* Environmental Science & Technology, 2003. **37**: p. 2486-2493.

36. Bennett, D.H. and E.J.Furtaw Jr., *Fugacity-based indoor residential pesticide fate model.* Environmental Science & Technology, 2004. **38**: p. 2142-2152.

37. Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden, *Environmental Organic Chemistry*. 1993, New York: John Wiley & Sons, INC.

38. Diamond, M.L., S.E. Gingrich, K. Fertuck, B.E. McCarry, G.A. Stern, B. Billeck, B. Grift, D. Brooker, and T.D. Yager, *Evidence for organic film on an impervious urban surface: Characterization and potential teratogenic effects.* Environmental Science & Technology, 2000. **34**(14): p. 2900-2908.

39. Lam, B., M.L. Diamond, A.J. Simpson, P.A. Makar, J. Truong, and N.A. Hernandez-Martinex, *Chemical composition of surface films on glass windows and implications for atmospheric chemistry.* Atmospheric Environment, 2005. **39**(35): p. 6578-6586.

40. Weschler, C.J., A. Wisthaler, S. Cowin, G. Tamas, P. Strom-Tejsen, A.T. Hodgson, H. Destaillats, J. Herrington, J. Zhang, and W.W. Nazaroff, *Ozone-initiated chemistry in an occupied simulated aircraft cabin.* Environmental Science & Technology, 2007. **41**(17): p. 6177-6184.

41. Harner, T. and T.F. Bidleman, *Octanol-air partition coefficient for describing particle/gas partitioning of aromatic compounds in urban air.* Environmental Science & Technology, 1998. **32**(10): p. 1494-1502.

42. Cousins, I.T. and D. Mackay, *Gas-particle partitioning of organic compounds and its interpretation using relative solubilities.* Environmental Science & Technology, 2001. **35**(4): p. 643-647.

43. Maddalena, R., T.E. McKone, and N.Y. Kado, *Exposure chamber measurements of mass transfer and partitioning at the plant/air interface.* Environmental Science & Technology, 2002. **36**(16): p. 3577-3585.

44. FAA, *200705utilization.pdf.*

45. Baker, S.E., A.O. Olsson, and D.B. Barr, *Isotope Dilution High-Performance Liquid Chromatography–Tandem Mass Spectrometry Method for Quantifying Urinary Metabolites of Synthetic Pyrethroid Insecticides.* Archives of Environmental Contamination and Toxicology, 2004. **46**(3): p. 281-288.

46. Shan, G., H. Huang, D.W. Stoutamire, S.J. Gee, G. Leng, and B.D. Hammock, *A sensitive class specific immunoassay for the detection of pyrethroid metabolites in human urine.* Chemical Research in Toxicology, 2004. **17**: p. 218-225.

47. Leng, G. and W. Gries, *Simultaneous determination of pyrethroid and pyrethrin metabolites in human urine by gas chromatography-high resolution mass spectrometry.* Journal of Chromatography B, 2005. **814**: p. 285-294.

48. Leng, G., E. Berger-Preiβ, K. Levsen, U. Ranft, D. Sugiri, W. Hadnagy, and H. Idel, *Pyrethroids used indoor - ambient monitoring of pyrethroids following a pest control operation.* International Journal of Hygiene and Environmental Health, 2005. **208**: p. 193-199.

49. Carlson, D.A., J.A. Hogsette, D.L. Kline, C.D. Geden, and R.K. Vandermeer, *Prevention of mosquitoes (Diptera: Calicidar) and house flies (Diptera: Muscidar) from entering simulated aircraft with commercial air curtain units.* Journal of Economic Entomology, 2006. **99**(1): p. 182-193.

50. Tatem, A.J., D.J. Rogers, and S.I. Hay, *Estimating the malaria risk of Africa mosquito movement by air travel.* Malaria Journal (open access), 2006. **5**(57).